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CYCLOHEPTATRIENYL BRIDGED RUTHENIUM AND RHODIUM COMPLEXES

by

VASUDEVAMURTHY ACHUTHA

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

FALL 1986

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in partial fulfilment of the requirements for the degree of MASTER OF SCIENCE

Supervisor

DATE Oct 1, 1986

ABSTRACT

The research work described here was undertaken to prepare cycloheptatrienyl bridged ruthenium-rhodium complexes and to study their substitution reactions.

A convenient, high yield synthetic method for the preparation of the starting material for this project $(\eta^4\text{-}C_7H_8)Ru(CO)_3$, **1**, is described. Entry into hetero-bimetallic complexes is achieved by preparing the precursor complex $(\eta^3\text{-}C_7H_7)Ru(CO)_3^-$, **2**, by deprotonation of compound **1**. Reaction of **2** with $[Rh(COD)Cl]_2$ gives $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(COD)$, **3**, in moderate yields. The solid state structure of **3** has been determined. It shows the expected cis-disposition of the Ru and Rh atoms, the bridging cycloheptatrienyl moiety bonded in a η^4-fashion to Rh and via η^3-allyl fragment to Ru. The orientation of the COD ligand on Rh gives this centre the usual square pyramidal geometry seen in $Rh(diene)_2L$ complexes.

Complex **3** undergoes facile carbonylation to produce $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2$, **4**. Complex **4** reacts readily with phosphines to give the monosubstituted $(\mu\text{-}C_7H_7)(\mu\text{-}CO)Ru(CO)_2Rh(CO)(PPh_3)$, **5** and disubstituted $(\mu\text{-}C_7H_7)(\mu\text{-}DPPM)Ru(CO)_2Rh(CO)$, **6** complexes. The presence of a bridging carbonyl group in **5** implies a reversal of the bonding mode of the $(\mu\text{-}C_7H_7)$ moiety from η^3-Ru, η^4-Rh in **4** to η^4-Ru, η^3-Rh in **5**. Variable temperature ^{13}C NMR

spectra showed that all these complexes are fluxional.

The ready formation of compound **6** containing the bridging DPPM unit in hydrocarbon solvents is in contrast with its Fe-Rh analogue where a chelating DPPM was isolated first which then slowly converted into the bridging DPPM isomer. Variable temperature ^{31}P NMR studies were carried out to identify possible intermediates in the reaction of complex **4** with DPPM. A scheme is proposed for the reaction pathway.

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LIST OF ABBREVIATIONS

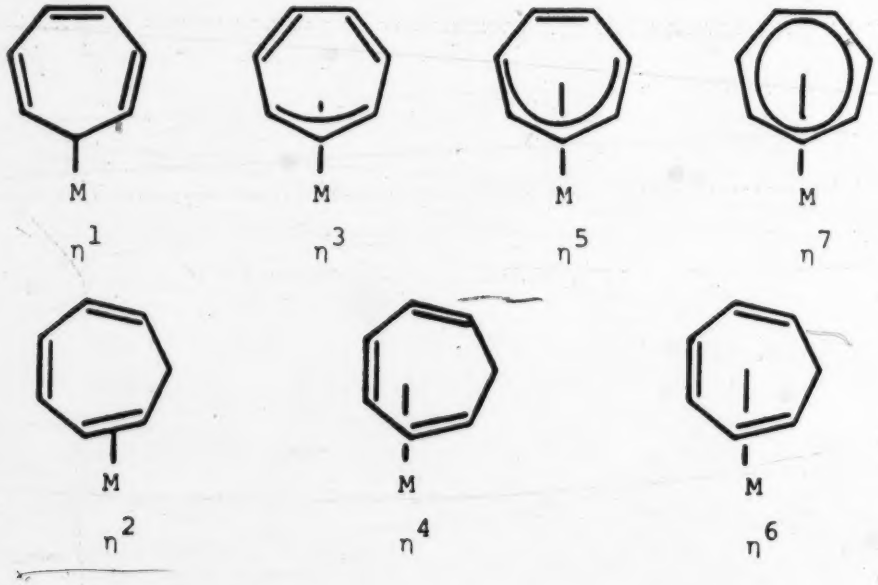
CHT	1,3,5-Cycloheptatriene
COD	1,5-Cyclooctadiene
COT	Cyclooctatetraene
Cp	η^4-Cyclopentadienyl, C_5H_5
DPPM	Bis(diphenylphosphino)methane
Me	Methyl, CH_3
n-Bu	n-Butyl, C_4H_9
Ph	Phenyl, C_6H_5
PPh_3	Triphenylphosphine
^tBu	tertiary butyl, C_4H_9

CHAPTER 1

INTRODUCTION

A. The Cycloheptatrienyl (C_7H_7) and Cycloheptatriene (C_7H_8) Ligand Systems

The cycloheptatrienyl (C_7H_7) moiety and the parent cycloheptatriene (C_7H_8) are versatile ligands which due to the presence of three conjugated double bonds are capable of bonding to different transition metals employing from one to seven carbon atoms.[1] A schematic representation of the different bonding modes is shown below, utilizing the hapto (abbreviated by the η designation) nomenclature first introduced by Cotton.[2]



In addition to forming mononuclear complexes, the ligands are also known to bridge two transition metals together thereby extending the range of complexes and the versatility of the ligand system.

B. Tetrahaptocycloheptatriene(tricarbonyl)iron, (1-4-η-C_7H_8)$Fe(CO)_3$ - The Quintessential Cycloheptatriene Metal Carbonyl Complex

The reaction of cycloheptatriene (CHT) with group VI transition metal carbonyls was one of the first reactions carried out in "modern" organometallic chemistry[3,4] (eq. 1)

$$M(CO)_6 + C_7H_8 \xrightarrow{\text{heat}} M((1\text{-}6\text{-}\eta\text{-}C_7H_8)(CO)_3 \quad (M = Cr, Mo, W) \qquad (1)$$

In these complexes the metal atom attains the formal inert gas electronic configuration by use of π-electrons from all three double bonds of cycloheptatriene. By analogy (η^6-C_7H_8)$Fe(CO)_2$ could be expected from the reaction of $Fe(CO)_5$ with cycloheptatriene. The thermal reaction between $Fe(CO)_5$ and CHT was first carried out by Wilkinson[5] who indeed formulated the isolated compound as shown above. However, subsequent studies of this

compound, using IR and NMR techniques, showed that instead of a $Fe(CO)_2$ moiety the compound contained a $Fe(CO)_3$ group bonded to two adjacent double bonds of the triene, while the third double bond remained uncoordinated.[6] This demonstrates the pronounced tendency of the $Fe(CO)_3$ moiety to preferentially coordinate to conjugated 1-3 dienes.

This compound also provides an excellent example of modification of ligand properties and stabilization of reactive organic moieties via metal coordination.

Cycloheptatriene is an extremely weak protic acid with an estimated pK_a of 36.[7] In contrast the exo-hydrogen of $(CHT)Fe(CO)_3$ can be exchanged quantitatively by $NaOCH_3$ in CH_3OD at ambient temperature.[8] A similar reaction, carried out at elevated temperature for 24 hours, with cycloheptatriene did not result in detectable deuterium incorporation.[9]

The uncomplexed anion $C_7H_7^-$ is an antiaromatic 8π electron system and as expected is unstable and there is only limited indirect evidence for its existence.[9] On the other hand, the $(C_7H_7)Fe(CO)_3^-$ anion, albeit air sensitive, is thermally stable. The coordination of the $Fe(CO)_3$ group to the η^3-allyl part of the C_7H_7 ring has been verified by X-ray crystallography,[10] and put on firm theoretical basis by molecular orbital calculations.[11]

Research work from this laboratory[12] and elsewhere

has shown that the anion is an ambident nucleophile capable of reacting both at the iron centre and/or at the ring carbon atoms. Thus $(C_7H_7)Fe(CO)_3^-$ reacts with transition metal carbonyl halides to form heterobimetallic cycloheptatrienyl compounds of the type $(\mu\text{-}C_7H_7)Fe(CO)_3M(CO)_x$ (M = Mn, Re; x = 3, M = Rh; x = 2).[12]

In contrast, the reaction with Me_3SiCl and Me_3GeBr proceeds,[13] by carbon attack with concommitant formation of $[1\text{-}4\text{-}\eta\text{-}7(R_3E)(C_7H_7)]Fe(CO)_3$, (E = Si or Ge).

C. Polyolefin Bridged Heterobimetallic Compounds

Heterobimetallic complexes are of current interest and the chemistry of these complexes has been considerably developed in view of the potential use of such complexes in bimetallic activation reactions. It is hoped that some of these complexes will show special reactivity features as a result of cooperation between adjacent metal centres combining the different reactivity properties of the constituent metals. The low symmetry which heteronuclear compounds inherently possess has been shown to be extremely useful for elucidating specific sites of reactivity and can provide important insight into mechanistic details.[14]

Several synthetic routes have been explored to

synthesize these compounds. Particularly successful are those that rely on bridge-assisted reactions. Bridging groups are useful, since these ligands may prevent rearrangement of the metal centres during reactions. For example, the use of heterodifunctional ligands to link two different metal fragments has been employed frequently. Casey et al. have prepared a series of Rh-Mo and Ir-Mo compounds linked by the $C_5H_4PR_2$ ligand.[15] The use of phosphido, PR_2, ligands have been used by several groups and a recent example are complexes of general formula $(CO)_4 M(\mu\text{-}PCy_2)_2 M'(PPh_3)$ (M = Mo, W; M' = Ni, Pd, Pt).[16] Shaw et al. have demonstrated that the complexes of Pd, Pt, and Ir containing monodentate η^1-DPPM ligands (DPPM = bisdiphenylphosphinomethane) could lead to bis-DPPM bridged heterobimetallic compounds.[17] A similar method, using either $Ru(COD)(DPPM)_2$ (COD = 1,5-cyclo-octadiene) which contains a monodentate DPPM ligand, or the bis-chelated $RuH_2(DPPM)_2$ on treatment with $[Rh(CO)_2Cl]_2$ or $[Rh(COD)Cl]_2$ gave a variety of ruthenium-rhodium complexes containing mono- and bis-DPPM bridged complexes,[18] $(\mu\text{-DPPM})(\mu\text{-Cl})(\mu\text{-H})Ru(H)(DPPM)Rh(COD)$, and $(\mu\text{-DPPM})_2(\mu\text{-CO})Ru(CO)_2Rh(Cl)$.

Another interesting synthetic method utilizes polyolefin type ligands as bridging units. Attention was drawn to the fact that the flexible bonding capability of

the polyolefin ligands may open up reactivity centres in this type of compounds and thereby render them potential catalysts or catalyst precursors for important chemical transformations. This role of the polyolefin bridge was termed "incipient coordinative unsaturation".[19]

Some time ago in this laboratory, synthesis of the bridged complex $(\mu\text{-}C_7H_7)Fe(CO)_3Rh(CO)_2$ was reported and the easy $CO/^{13}CO$ exchange was attributed to facile bonding mode change of the $(\mu\text{-}C_7H_7)$ moiety.[12]

The work on bimetallic compounds containing bridging cyclooctatetrene (COT) moiety by Salzer[20a,b] provides another good example of fluxional heterobimetallic compounds akin to the cycloheptatrienyl bridged complexes referred to above. It was shown that the COT complexes $(\eta^4\text{-}C_8H_8)Fe(CO)_3$ or $(\eta^4\text{-}C_8H_8)M(Cp)$ (Cp = C_5H_5, M = Co, Rh), with two uncoordinated double bonds readily react with unsaturated organometallic species to yield bimetallic complexes in which both metals occupy the same face of a common fluxional cyclooctatetraene ligand. An example is given in equation 2.

$$(\eta^4\text{-}C_8H_8)Fe(CO)_3 + [Rh(COD)]BF_4 \rightarrow$$

$$[(\mu\text{-}C_8H_8)Fe(CO)_3Rh(COD)]BF_4 \qquad (2)$$

D. Scope of the Present Research

In view of the interesting properties exhibited by $(C_7H_7)Fe(CO)_3^-$ anion, it was considered worthwhile to investigate the reactivity of its ruthenium analogue, $(C_7H_7)Ru(CO)_3^-$. The synthetic routes to the preparation of the starting material, $(C_7H_8)Ru(CO)_3$, are rather cumbersome and/or of low yields, hence a more convenient and high yield procedure was needed. The synthetic method we are presenting in this work is promising.

The reactivity of the ruthenium anion toward $[Rh(COD)Cl]_2$ was carried out with the aim of preparing the ruthenium-rhodium bimetallic compounds and to study their substitution reactions. The substituted complexes are expected to show fluxional behaviour similar to the iron analogues and hence ^{13}C NMR studies were undertaken to explore this property.

CHAPTER 2

SYNTHESIS OF $(\eta^4\text{-}C_7H_8)Ru(CO)_3$ AND $(\eta^3\text{-}C_7H_7)Ru(CO)_3^-$

A. Preparation of $(\eta^4$-Cycloheptatriene)tricarbonyl ruthenium

1. Introduction

Although various synthetic routes have been reported for the synthesis of $(\eta^4$-cycloheptatriene)tricarbonyl ruthenium, **1**, a high yield procedure for this molecule at the start of this research was still lacking. Both thermal and photochemical reactions between $Ru_3(CO)_{12}$ and excess cycloheptatriene have been reported.[21] The thermal reaction gave a mixture of compounds. The major product was a trinuclear ruthenium species $Ru_3(CO)_6(C_7H_7)(C_7H_9)$, while compound **1** was only a minor component. Moreover the isolation of the compound via silica gel chromatography apparently resulted in extensive decomposition. The photochemical reaction in benzene was reported to give compound **1** in about 28% yield but only after prolonged photolysis. However due to contamination by unspecified hydrocarbon impurities, analytical data and reliable NMR spectra of compound **1** could not be obtained. In an effort to eliminate the formation of trinuclear ruthenium

species, the displacement of 1,5-cyclooctadiene (COD) from $Ru(CO)_3(COD)$ by cycloheptatriene was carried out. This reaction gave 1 only in low yield.[22] Finally prolonged atmospheric carbonylation of $Ru(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_8H_{10})$ (C_8H_{10} = 1,3,5-cyclooctatriene) at room temperature in the presence of excess cycloheptatriene gave a mixture of 1 and $Ru(CO)_2(\eta^6\text{-}C_7H_8)$.[23] Isolation of 1 was again problematic.

Of all the methods tried so far to prepare 1, the photochemical reaction appeared to hold the most promise for further refinements. This was the only method which yielded 1 free of multiple side products. A possible reason for the long reaction time and low yields may be the low solubility of $Ru_3(CO)_{12}$ in benzene at room temperature.

2. Results and Discussion

The photolysis of $Ru_3(CO)_{12}$ and cycloheptatriene was carried out at different temperatures. It was established that by running the reaction in benzene at approximately 70°C, up to 85% yields of 1 could be achieved, eq. 3.

$$Ru_3(CO)_{12} + \text{excess } C_7H_8 \xrightarrow[70^\circ C,\ 24\ h]{h\nu,\ \text{benzene}} \underset{85\%}{(C_7H_8)Ru(CO)_3} + Ru_3(CO)_6(C_7H_7)(C_7H_9) + \text{Ditropyl} + \text{Traces of other Ru species} \quad (3)$$

$$\underset{10\%}{}$$

The optimum temperature of 70°C was obtained by positioning the reaction vessel approximately 7 cm from the 450 W light source. The high temperature helps to dissolve completely the quantity of $Ru_3(CO)_{12}$ used in the preparation. Of course with the combination of thermal and photochemical reaction, the formation of side products could not be avoided. A major byproduct is the trinuclear compound $Ru_3(CO)_6(C_7H_7)(C_7H_9)$ species. This can be easily separated by silica gel chromatography. However trace amounts of other impurities, $Ru_2(CO)_6(C_7H_8)$, $Ru(CO)_3(C_7H_{10})$, and significant amounts of produced ditropyl (C_7H_7-C_7H_7) are rather difficult to remove. We found that traces of impurities in 1 do not significantly alter its reactivity. Analytically pure 1 can be obtained after repeated chromatography and precipitating the remaining impurities at low temperature (-78°C), but with significant reduction in the isolated yield.

(η^4-C_7H_8)$Ru(CO)_3$ is a pale yellow oil. The IR spectrum in the carbonyl region shows a three band pattern typical of a (diene)$M(CO)_3$ species. The positions at 2066(s), 2002(s), 1991(s) cm^{-1} agree with previously reported values.[21,22] The ^1H and ^{13}C NMR spectra of the compound are shown in Figure 1 and Figure 2.

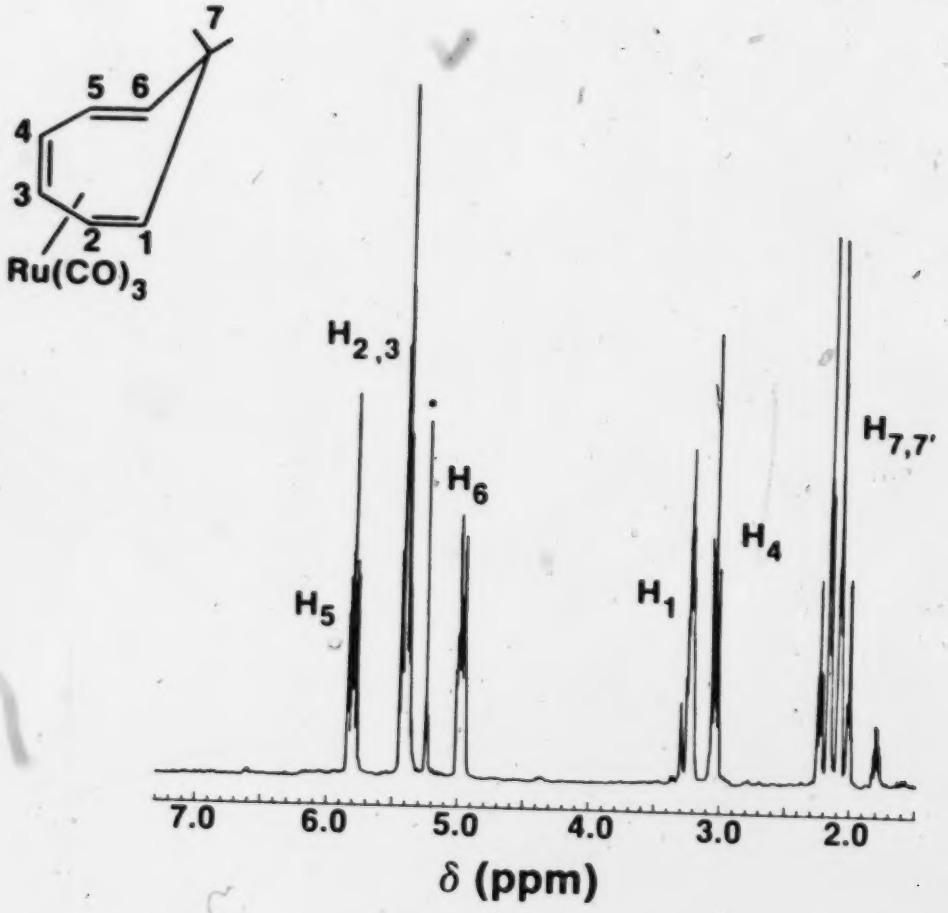


Figure 1. ^1H NMR Spectrum of $(\eta^4\text{-}C_7H_8)Ru(CO)_3$, 1. *$CHDCl_2$

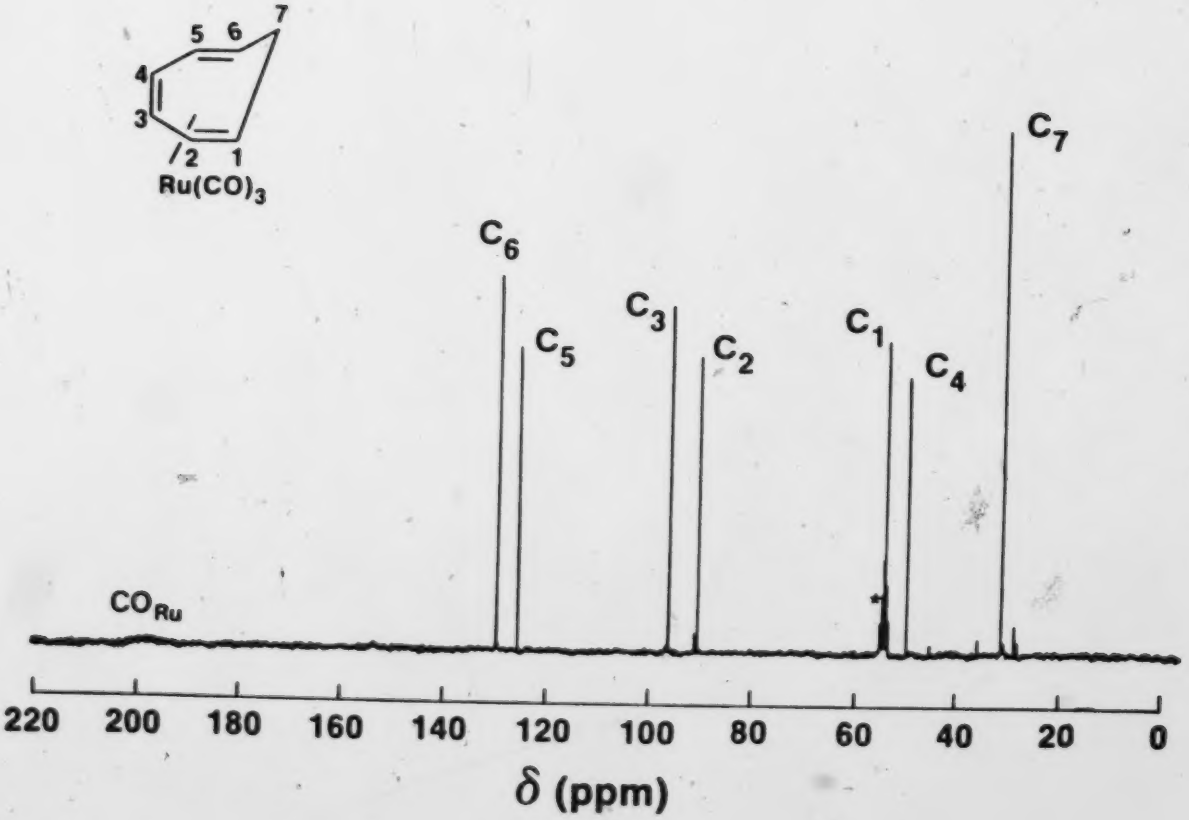


Figure 2. ^{13}C NMR Spectrum of $(\eta^4\text{-}C_7H_8)Ru(CO)_3$, 1. $^*CD_2Cl_2$

The coordination of the $Ru(CO)_3$ moiety in an 1-4-η fashion renders all hydrogen and carbon atoms of the ring inequivalent and this is most clearly seen in the ^{13}C NMR spectrum. The assignments appearing in the figures have been verified by decoupling experiments and correspond closely to the assignments in the analogous iron compound.[1] As expected from previous studies[24,25] the nuclei of the bound and diene fragment experience significant upfield chemical shifts from the free ligand values (Table 1). The coordination shifts are somewhat larger than in the corresponding iron analogue and most probably reflect a more significant π-back bonding to the ring in the present case.[26]

In the room temperature ^{13}C NMR spectrum of **1**, the carbonyl groups on Ru are seen as a barely discernible broad signal around 200 ppm. This is inconsistent with the expected square pyramidal geometry of **1** for which three peaks should be found. Three resonances in the ratio 1:1:1 at 196.3, 196.8, and 200.72 ppm are indeed present at -20°C. The molecule, like many other (diene)$M(CO)_3$ type compounds[27] is thus fluxional. The broad signal indicates rapid scrambling of the carbonyl groups at room temperature.

Table 1. ^{1}H and ^{13}C NMR Chemical Shift Data for $(\eta^4\text{-}C_7H_8)Ru(CO)_3$, 1.[a]

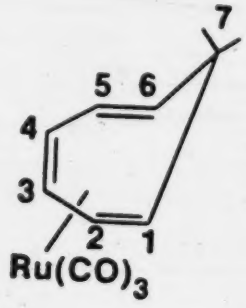
	δ (^{1}H)[b]	δ (^{13}C)	$\Delta\delta$[c]
H(1)/C(1)	3.25	53.3	77.2 (2.03)
H(2)/C(2)	5.4	90.3	36.5 (0.72)
H(3)/C(3)	5.45	95.6	35.4 (1.10)
H(4)/C(4)	3.15	49.4	81.6 (3.40)
H(5)/C(5)	5.8	125.2	1.6
H(6)/C(6)	5.0	129.1	-8.8
H(7)/C(7)	2.0-2.2	30.7	2.5

[a]Chemical shifts in ppm from TMS, solvent CD_2Cl_2.

[b]All signals are multiplets.

[c]$\Delta\delta$ = coordination shift = $\delta_{complex} - \delta_{free,C_7H_8}$. Chemical shifts of free C_7H_8 from reference 35 are: ^{1}H: H(1)/H(6) 5.28; H(2)/H(5) 6.12; H(3)/H(4) 6.55; H(7) 2.20. ^{13}C: C(1)/C(6) 120.5; C(2)/C(5) 126.8; C(3)/C(4) 131.0; C(7) 28.2. When relevant, the ^{1}H coordination shifts are in parentheses.

Assignments:



B. Deprotonation of $(\eta^4\text{-}C_7H_8)Ru(CO)_3$

1. Introduction

As indicated in the previous chapter, coordination of cycloheptatriene to a $Fe(CO)_3$ fragment results in a dramatic increase in the protic acidity of the polyene and $(\eta^4\text{-}C_7H_8)Fe(CO)_3$ can be quantitatively deprotonated by a variety of strong bases to give $(\eta^3\text{-}C_7H_7)Fe(CO)_3^-$, eq. 4.

$$(\eta^4\text{-}C_7H_8)Fe(CO)_3 \xrightarrow[\text{Solvent}]{\text{Base}} (\eta^3\text{-}C_7H_7)Fe(CO)_3^- \qquad (4)$$

yellow — deep red

Base:	Li^nBu/-60°C,	KH/r.t,	KO^tBu/r.t,	$NaN(SiMe_3)_2$/r.t
Solvent:	THF,	THF,	THF,	benzene
Reference:	(8),	(24),	(28),	(10)

Characteristic color change accompanies the deprotonation reaction. The ease of formation and relative stability of the anion demonstrates the stabilizing influence of the coordinated $Fe(CO)_3$ unit upon the organic moiety.

Research work from this laboratory has shown that the anion is a very versatile entry into a variety of cycloheptatrienyl-based organometallic compounds. The anion can be considered as an ambident nucleophile capable of reacting both at the iron centre and/or at the ring carbon atoms.[12,13]

It was clearly of interest to establish whether compound 1 will undergo facile deprotonation as well.

2. Results and Discussion

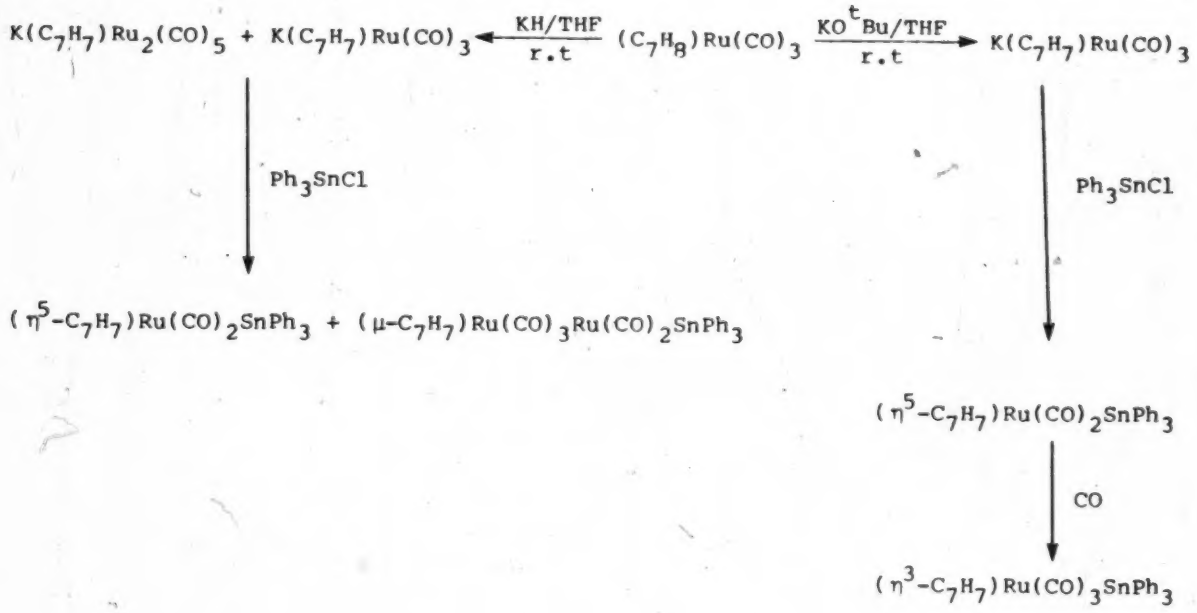
Contrary to the iron case, the deprotonation of 1 appears to be highly base dependent. KH was a useful reagent to prepare $K(C_7H_7)Fe(CO_3)$. However, in the present instance, a complicated behavior was seen. Although anionic species were formed, on the basis of further reaction with Ph_3SnCl, it appears that both mono- and bimetallic cycloheptatrienyl type compounds, $(\eta^3\text{-}C_7H_7)Ru(CO)_3^-$ and $(C_7H_7)Ru_2(CO)_5^-$, are obtained (Scheme 1).[29]

Deprotonation of 1 with KO^tBu proceeds without difficulty. The reaction is instantaneous and complete conversion to the anion was seen in a matter of minutes, eq. 5

$$\underset{\mathbf{1}}{(\eta^4\text{-}C_7H_8)Ru(CO)_3} \xrightarrow[THF/-78^0C]{KO^tBu} \underset{\mathbf{2}}{K(\eta^3\text{-}C_7H_7)Ru(CO)_3} + {}^tBuOH \qquad (5)$$

The appearance of the characteristic red colouration of the anion is seen upon addition of KO^tBu to the solution of 1 in THF. The formation of the anion can be easily followed by infrared spectroscopy. The absorption bands

Scheme 1. Preparation of $C_7H_7Ru(CO)_3^-$ and Its Reaction Toward Ph_3SnCl.



in the carbonyl region for compound **1** rapidly decrease, while new bands at 1959(s,br), 1886(s,br), 1864(sh) cm^{-1} appear. The decrease in carbonyl stretching frequencies is indicative of increased back bonding from ruthenium to the antibonding π^* molecular orbitals of the carbonyl moieties, and is in accord with the formulation of **2** as an anionic species. The ^1H NMR spectrum of **2** shows a sharp single peak for the seven ring protons even at -70°C, indicating rapid ring whizzing. High fluxionality was also observed for the analogous anionic iron complex.

C. Conclusion

The synthetic method described for the preparation of $(\eta^4\text{-}C_7H_8)Ru(CO)_3$ **1** is significant over previous syntheses and gives **1** in good yield. The deprotonation of **1** is base-dependent, however, the use of KO^tBu gives $(\eta^3\text{-}C_7H_7)Ru(CO)_3^-$ exclusively.

CHAPTER 3

REACTIVITY OF $(\eta^3\text{-}C_7H_7)Ru(CO)_3$ ANION: SYNTHESIS OF $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(L_2)$, L_2 = COD or L = CO

A. Introduction

The synthetic utility of $(C_7H_7)Fe(CO)_3^-$ has been demonstrated by its reaction with a variety of metal carbonyl halides to form heterobimetallic complexes of the type $(\mu\text{-}C_7H_7)Fe(CO)_3M(CO)_y$ (M = Mn or Re and y = 3, M = Rh and y = 2).[12] Although potentially useful, the method was synthetically disappointing due to undesirable side reactions resulting in overall low yields of the bimetallic products.

Recent work has revealed that, in the rhodium case, a two-step procedure involving first the preparation of $(\mu\text{-}C_7H_7)Fe(CO)_3Rh(COD)$ followed by atmospheric carbonylation resulted in dramatic improvement of the yield[30] (overall 65%). This allowed the synthesis of sufficient quantities of this interesting compound to begin exploring its chemistry. A similar approach to the synthesis of the Ru-Rh compound was followed and the results are described in this chapter.

B. Synthesis and Characterization of (μ-Cycloheptatrienyl)tricarbonylruthenium(cyclooctadiene)rhodium

Treatment of $(\eta^3\text{-}C_7H_7)Ru(CO)_3^-$ with 0.5 equivalent of $[Rh(COD)Cl]_2$ at room temperature in THF gave after simple work up and silica gel chromatography, a red crystalline material in moderate (30%) yield. Elemental analysis and spectroscopic data on the compound are consistent with the formulation $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(COD)$, **3** (eq. 6).

$$\underset{\mathbf{2}}{K(C_7H_7)Ru(CO)_3} + 1/2\ [Rh(COD)Cl]_2 \xrightarrow{THF}$$

$$\underset{\mathbf{3}}{(C_7H_7)Ru(CO)_3Rh(COD)} + KCl \qquad (6)$$

The mass spectrum shows the parent molecule ion followed by the successive loss of three carbonyl groups. The infrared spectrum exhibits two strong absorption bands in the terminal carbonyl region at 2029 and 1965 cm^{-1} due to the $Ru(CO)_3$ moiety.

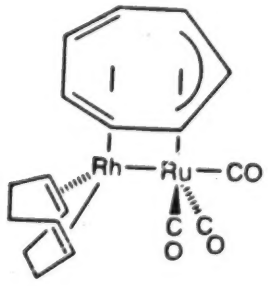
The ^1H NMR spectrum at room temperature shows a sharp singlet for the C_7H_7 moiety, a broad signal for the olefinic hydrogens and two multiplets for the aliphatic CH_2 groups of the COD ligand. The ^{13}C NMR spectrum shows a single line for the C_7H_7 moiety, a singlet for the

aliphatic carbons of COD ligand and only one resonance for the three carbonyl groups on ruthenium. The olefinic carbons appear as a sharp doublet (J_{Rh-C} = 9.2 Hz) conclusively demonstrating that the COD ligand remains bonded to the Rh atom. The NMR data are clearly irreconcilable with a rigid bonding between the bridging C_7H_7 ligand and the Ru-Rh fragment, but can be explained in terms of rapid rotation of the cycloheptatrienyl moiety about the two attached metal centres. Such motion results in a single time averaged environment for all the seven carbon atoms of the ring. The limiting spectrum could not be reached even at -80°C. This is a general phenomenon observed for cis-bimetallic derivatives of conjugated cyclic polyolefins.[31] The activation barrier for internal reorientation of the bridging polyolefin is much smaller than for the related trans complexes. For example, in the analogous Fe-Rh compound the limiting spectrum could not be reached even at -164°C,[12] while the limiting spectrum of trans-$[(C_5H_5)(CO)_2Mo(C_7H_7)Fe(CO)_3]$ was already reached at -71°C.[31] Several other organometallic derivatives containing the cycloheptatrienyl and cyclooctatetraene ligands exhibit this type of fluxional behaviour.[27]

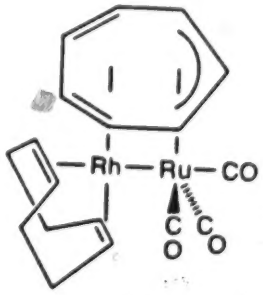
The observation of only two and three signals for the COD ligands in the ^{13}C and ^{1}H NMR spectra respectively at room temperature, is not in agreement with rigid bonding

mode of this ligand either. The simplified spectra can also be explained in terms of rapid rotation of the COD ligand about Rh. As the temperature is lowered one of the averaged CH_2 signals in the ^1H NMR spectrum clearly splits into two broad unresolved peaks, indicating the slowing down of the COD rotation about the rhodium atom. The signal due to the other CH_2 group undergoes a slight broadening. The behaviour of olefinic protons does not change much. However the ^{13}C NMR, Figure 3, gives a clearer picture. At -30°C, two doublets for the coordinated olefinic carbons and two singlets for the two different types of aliphatic carbon atoms are seen. The free energy of activation ($\Delta G^{\ddagger}_{T_c}$, T_c = coalescence temperature) for COD rotation at -10°C is 12.6 kcal/mol.[32]

Two structural forms, A and B, can be drawn for this compound, both are in agreement with the observed NMR features.



A



B

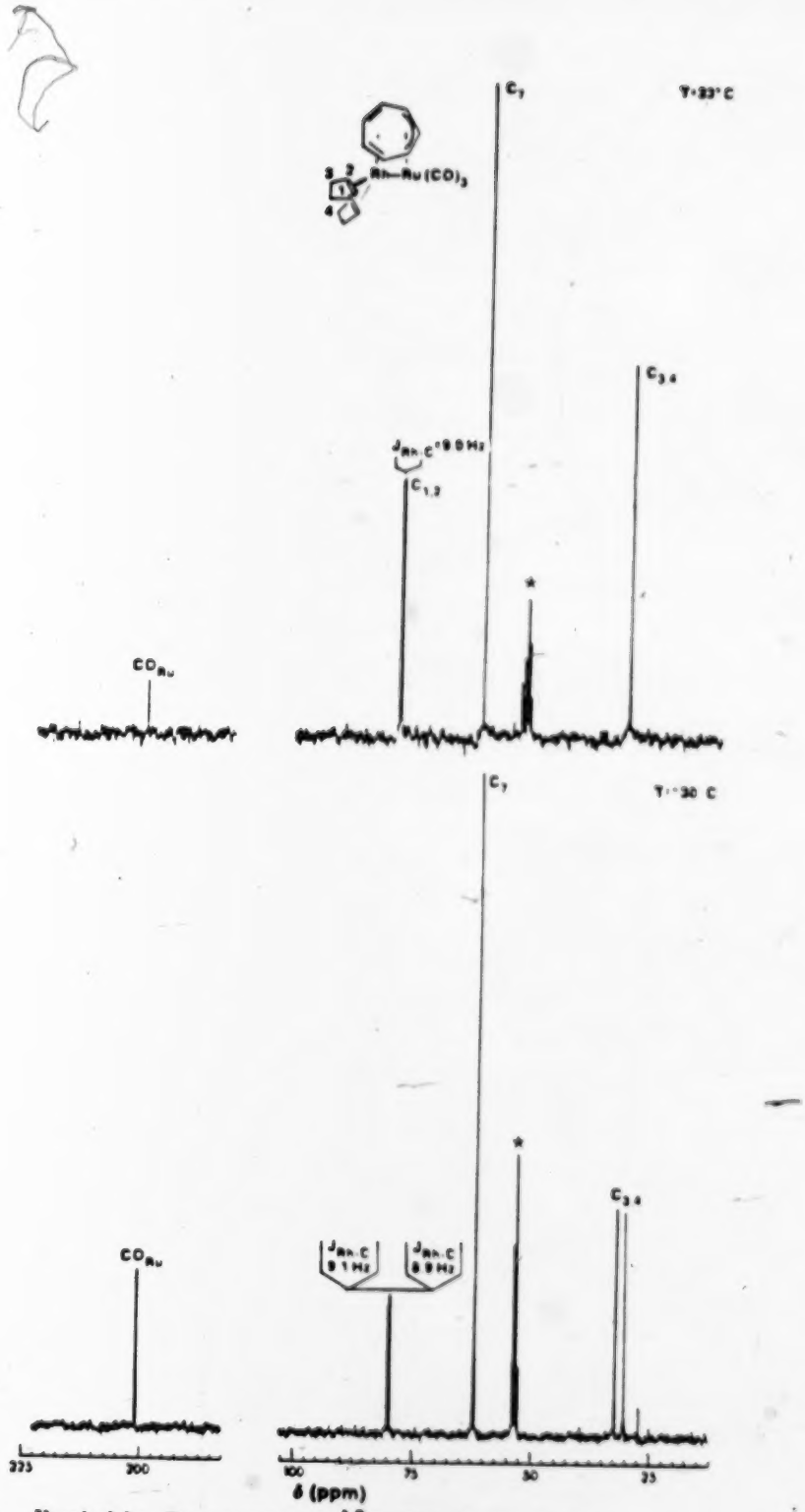


Figure 3. Variable Temperature ^{13}C NMR Spectra of $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(COD)$, 3. $^{*}CD_2Cl_2$.

In A the double bonds occupy equivalent coordination sites on the rhodium trans to the bridging C_7H_7 ring and the geometry of Rh atom is square pyramidal. In B the COD ligand occupies non-equivalent coordination sites, one double bond being trans to the Ru-Rh bond and the other trans to the C_7H_7 ring and the geometry of Rh atom is triagonal bipyramid. In both instances the molecule possesses C_s symmetry and results in distinct olefinic and aliphatic carbon atoms as seen at low temperature in the ^{13}C NMR spectrum.

Single crystal X-ray structure determination was carried out to establish the ground state structure of the molecule. A perspective view of the molecule together with atom numbering scheme is shown in Figure 4 and relevant bond distances and angles are listed in Table 2 and Table 3.

The X-ray structure clearly shows that the molecule contains the cis disposition of the Rh and Ru atoms. Three of the ring carbon atoms form effectively a π-allyl group directly bonded to the Ru atom. The other four ring carbon atoms are substantially co-planar and are directly bonded the Rh atom. The ruthenium atom is also bonded to the three carbonyl groups and to rhodium. Two of the carbonyl moieties are trans to the allyl group while the other CO is trans to the Ru-Rh bond. The rhodium centre,

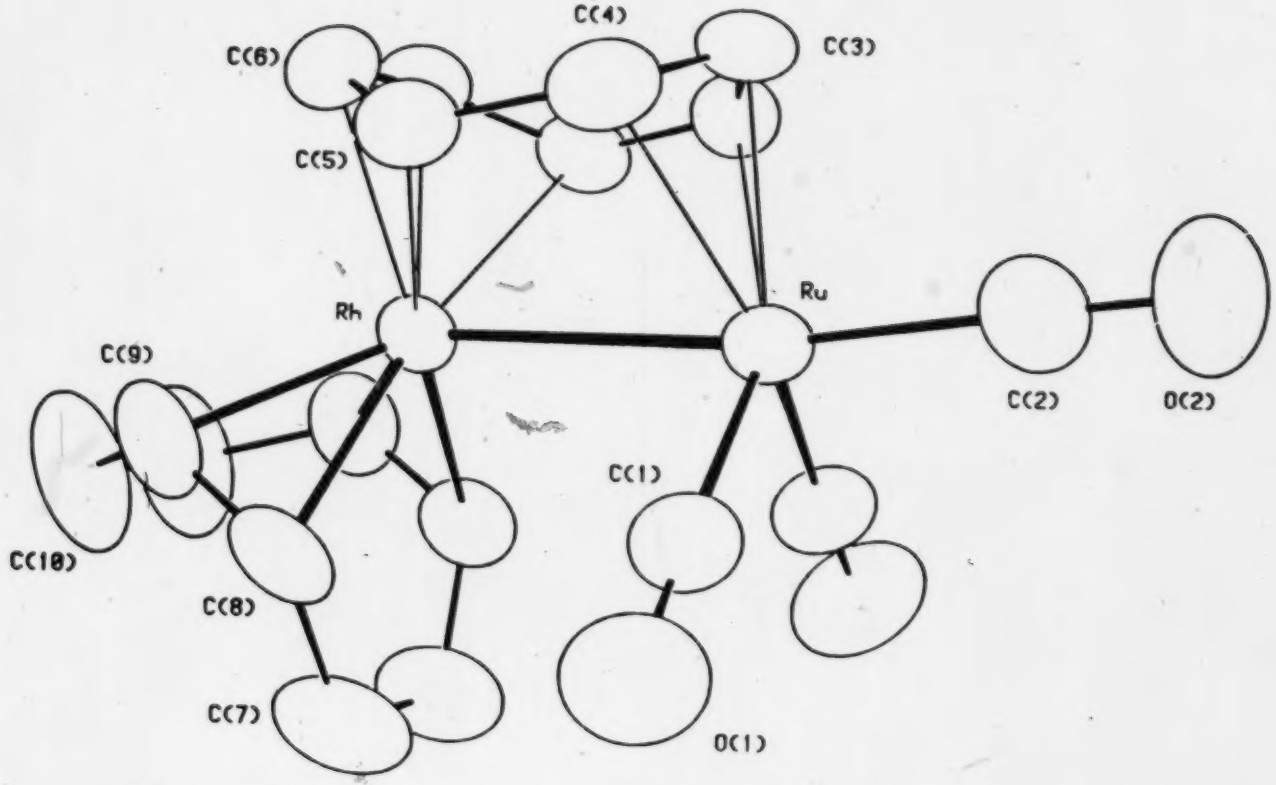


Figure 4. X-ray Molecular Structure of $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(COD)$, 3.

Table 2. Table of Bond Distances in Angstroms in $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(COD)$, 3.

Atom1	Atom2	Distance	Atom1	Atom2	Distance	Atom1	Atom2	Distance
Rh	Ru	2.8878 (6)	Ru	C(3)	2.159 (5)	C(6)	C(6)'	1.384 (8)
Rh	C(5)	2.207 (3)	Ru	C(4)	2.273 (3)	C(7)	C(7)'	1.50 (1)
Rh	C(6)	2.174 (3)	O(1)	C(1)	1.141 (5)	C(7)	C(8)	1.507 (6)
Rh	C(8)	2.176 (3)	O(2)	C(2)	1.128 (7)	C(8)	C(9)	1.386 (6)
Rh	C(9)	2.174 (4)	C(3)	C(4)	1.388 (5)	C(9)	C(10)	1.522 (6)
Ru	C(1)	1.896 (4)	C(4)	C(5)	1.450 (5)	C(10)	C(10)'	1.42 (1)
Ru	C(2)	1.896 (6)	C(5)	C(6)	1.423 (5)			

Numbers in parentheses are estimated standard deviations in the least significant digits.

The ' indicates atoms related by the mirror plane.

Table 3. Table of Bond Angles in Degrees in $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(COD)$, 3.

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Ru	Rh	C(5)	70.9 (1)	C(1)	Ru	C(2)	96.4 (2)	Rh	C(5)	C(6)	69.8 (2)
Ru	Rh	C(6)	100.0 (1)	C(1)	Ru	C(3)	132.9 (1)	C(4)	C(5)	C(6)	127.4 (4)
Ru	Rh	C(8)	97.7 (1)	C(1)	Ru	C(4)	98.0 (2)	Rh	C(6)	C(5)	72.3 (2)
Ru	Rh	C(9)	131.2 (1)	C(2)	Ru	C(3)	87.3 (2)	C(5)	C(6)	C(6)'	121.6 (2)
C(5)	Rh	C(6)	37.9 (1)	C(2)	Ru	C(4)	102.8 (2)	C(7)'	C(7)	C(8)	116.4 (2)
C(5)	Rh	C(8)	97.5 (1)	C(3)	Ru	C(4)	36.4 (1)	Rh	C(8)	C(7)	111.3 (3)
C(5)	Rh	C(9)	93.2 (1)	Ru	C(1)	O(1)	178.1 (4)	Rh	C(8)	C(9)	71.4 (2)
C(6)	Rh	C(8)	117.7 (1)	Ru	C(2)	O(2)	179.1 (6)	C(7)	C(8)	C(9)	125.2 (4)
C(6)	Rh	C(9)	92.1 (2)	Ru	C(3)	C(4)	76.3 (2)	Rh	C(9)	C(8)	71.5 (2)
C(8)	Rh	C(9)	37.2 (2)	C(4)	C(3)	C(4)'	121.9 (5)	Rh	C(9)	C(10)	110.9 (3)
Rh	Ru	C(1)	89.1 (1)	Ru	C(4)	C(3)	67.3 (2)	C(8)	C(9)	C(10)	124.8 (5)
Rh	Ru	C(2)	172.0 (2)	Ru	C(4)	C(5)	105.6 (2)	C(9)	C(10)	C(10)'	117.4 (3)
Rh	Ru	C(3)	84.6 (1)	C(3)	C(4)	C(5)	124.9 (4)				
Rh	Ru	C(4)	70.5 (1)	Rh	C(5)	C(4)	109.7 (2)				

Numbers in parentheses are estimated standard deviations in the least significant digits.

The ' indicates atoms related by the mirror plane.

besides bonding to the Ru and to the diene part of the carbocycle, is also attached to the olefinic carbons of the COD ligand. The Ru-Rh bond distance is 2.8876(6) Å.

The distance between ruthenium and the central carbon atom of the π-allyl group is 2.159(5)Å. This is significantly shorter than the distance to the end carbon atoms (2.273(3)Å) and is consistent with the usual observation in π-allyl metal compounds. For example in $Ru_2(CO)_5(SiMe_3)(C_7H_6SiMe_3)$ (Me = CH_3), the Ru to central allyl carbon atom separation is 2.170(12)Å while that to the end carbon atom is 2.286(11)Å.[33] The C-C distances within the π-allyl fragment are 1.388(5)Å, which is comparable to many previously reported values (1.38-1.42Å).

The geometry of the five coordinate rhodium in this compound is square pyramidal and not the alternate trigonal bipyramidal. This is the observed geometry in the related compounds $(\mu\text{-}C_7H_7)Rh(COD)Fe(CO)_3$[30] and $(\mu\text{-}C_7H_7)Rh(CO)_2Fe(CO)_3$.[12] The rhodium to 1-4-η-diene carbon atom distances, 2.207(3)Å and 2.174(3)Å to the outer and inner carbon atoms respectively, are typical.

Thus the X-ray structure determination demonstrates that the ground state structure of **3** is represented by form A, with η^3-Ru and η^4-Rh coordination of the two metals. Both metals achieve the noble gas electronic configuration through a metal-metal bond and a bridging fluxional carbocyclic ligand.

C. Synthesis and Characterization of (μ-Cycloheptatrienyl)tricarbonylruthenium(dicarbonyl)rhodium

As observed in the case of the analogous Fe-Rh complex the COD ligand of $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(COD)$ **3** is quite labile and can be easily replaced by carbon monoxide. The reaction of compound **3** with CO at room temperature and atmospheric pressure is quite rapid and results in the formation of $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2$ **4** in quantitative yield, eq. 7

$$\underset{\mathbf{3}}{(\mu\text{-}C_7H_7)Ru(CO)_3Rh(COD)} + CO \xrightarrow[RT]{\text{hexane}} \underset{\mathbf{4}}{(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2} + COD \qquad (7)$$

Compound **4** is a red solid. Its mass spectrum shows the parent molecular ion M^+ and successive loss of five carbonyl groups. The infrared spectrum shows five carbonyl bands at 2064(s), 2023(s), 2004(s), 1979(s), and 1965(m) cm^{-1} consistent with the low molecular symmetry (C_s) and the presence of only terminal carbonyl groups.

At room temperature the ^{13}C NMR spectrum, Figure 5, shows a sharp signal for the C_7H_7 ring and in the carbonyl region, the $Rh(CO)_2$ fragment is seen as a doublet (J_{Rh-C} = 72 Hz) while the $Ru(CO)_3$ moiety is observed as a sharp singlet. The single peak observed for C_7H_7 ring is not surprising and is diagnostic of a rapidly whizzing cycloheptatrienyl ring. The signal broadens as the temperature is lowered but remains a single signal even at -78°C.

The single carbonyl signal for the CO groups on the ruthenium indicates local scrambling. The process is facile, since it still operates at the low temperature of -78°C. This feature is observed in many related compounds such as $(\mu\text{-}C_7H_7)Fe(CO)_3Rh(CO)_2$[12] and $(\mu\text{-}C_7H_7)Mn(CO)_3Fe(CO)_3$.[12]

The observation of distinct signals for the carbonyls on ruthenium and rhodium at room temperature indicates that no carbonyl exchange is occurring between the two metal centres. However, as the temperature is increased, Figure 5, the carbonyl resonances broaden, coalesce at around 45°C and reappear as a broad single peak at +70°C. Unfortunately a good high temperature limiting spectrum could not be obtained as the compound decomposed above 70°C. An approximate value for the free energy of activation for intermetallic CO exchange is 15.1 kcal/mol. The intermetallic carbonyl exchange can occur by a doubly bridged or single carbonyl bridged

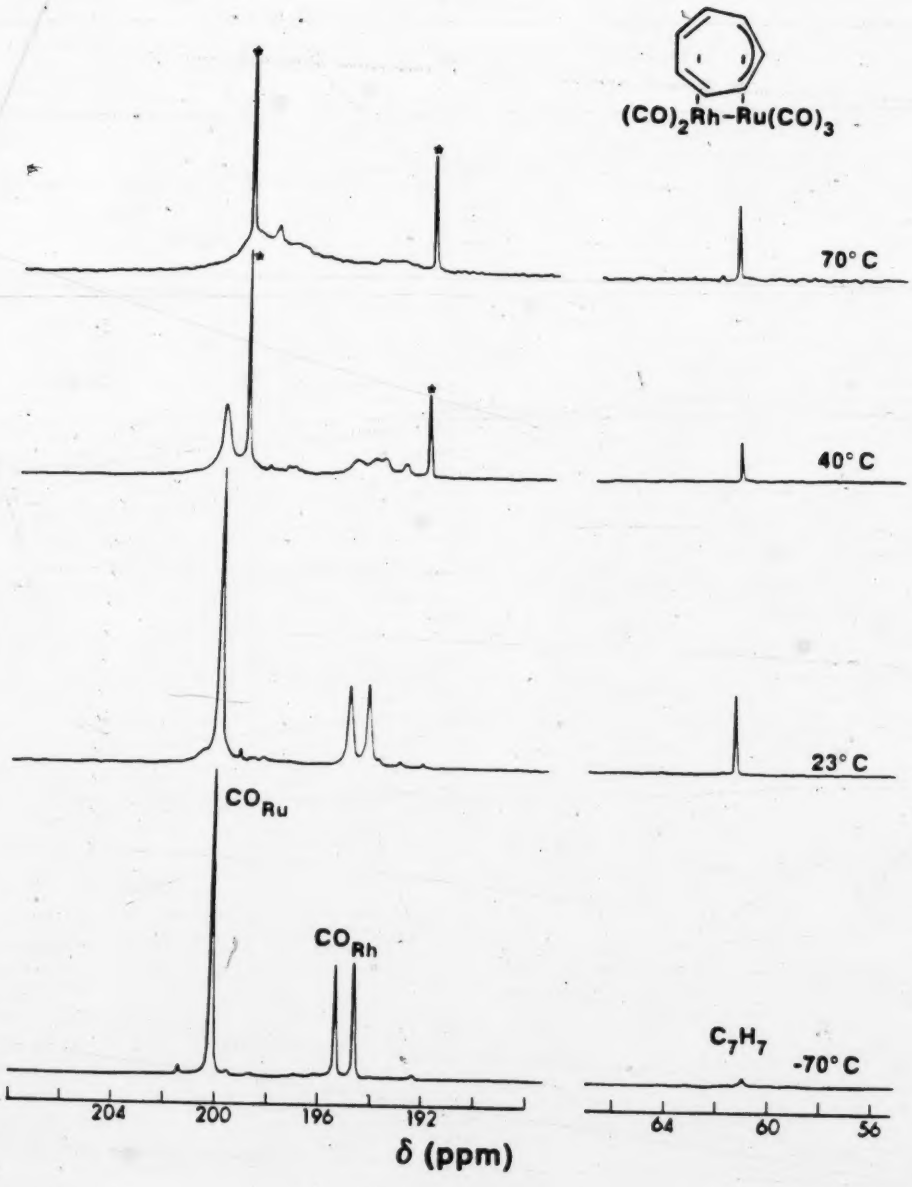
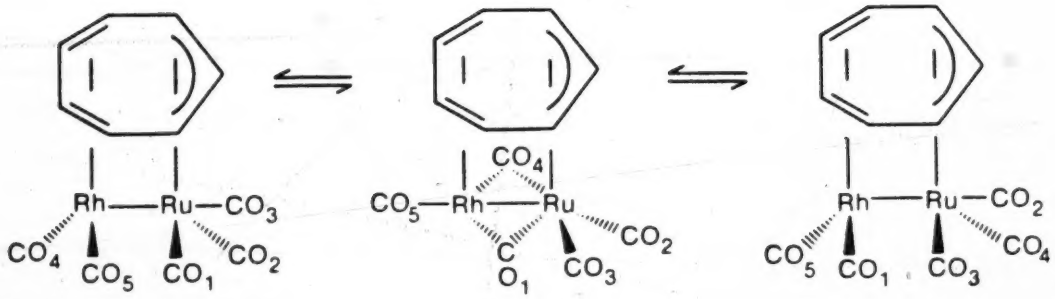


Figure 5. Variable Temperature ^{13}C NMR Spectra of $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2$, 4. *Decomposition products.

intermediate. The doubly bridged intermediate, Scheme 2, is favoured since it maintains the ground state μ-η^4(Rh), η^3(Ru)-C_7H_7 bonding mode and is similar to the often observed merry-go-round mechanism for carbonyl group migration in di- and polynuclear metal carbonyl compounds.[34]

Scheme 2. Intermetallic CO Exchange in Compound 4 Double Bridged Intermediate.



CHAPTER 4

SUBSTITUTION REACTIONS OF $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2$, 4

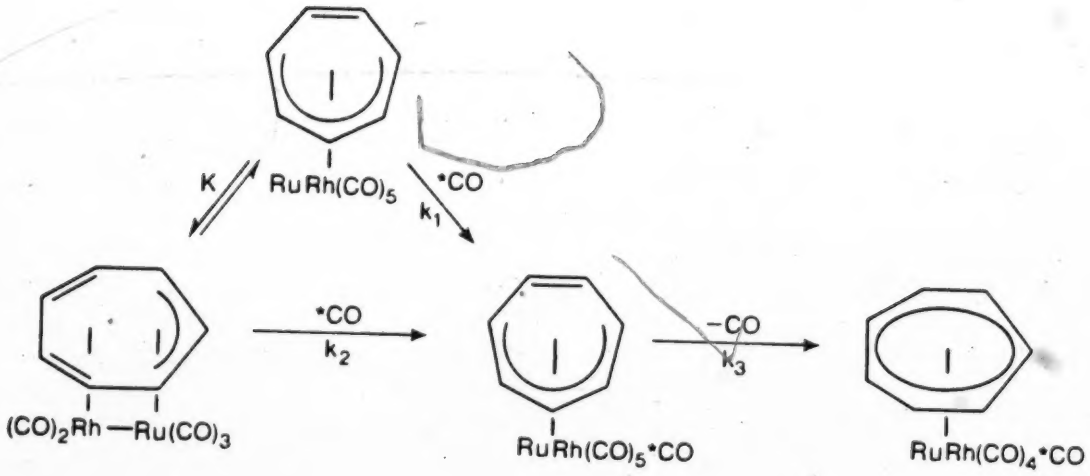
A. Introduction

It has been observed in the case of the analogous iron derivative[30] that the presence of the bridging cycloheptatrienyl moiety opened up reaction pathways which allowed for facile carbonyl substitution reactions to take place. The flexible bonding capability of the bridging seven membered ring was assumed to be responsible for the ease of these reactions.

Similar high reactivity was predictable for the present complex on the basis of the ready, non-discriminate and high level of ^{13}CO enrichment at room temperature and under atmospheric pressure conditions. The rapid carbonyl exchange must proceed through a $16e^-$ intermediate which, as in the case of the Fe-Rh complex, most probably proceeds by a bonding mode change of the cycloheptatrienyl ligand (Scheme 3).

In the proposed mechanism the ready accessibility of an intermediate with increased carbonyl content and a bridging cycloheptatrienyl unit of reduced η^5-hapticity is invoked. This intermediate could arise either by a rapid

Scheme 3. Pathway for ^{13}CO Enrichment of Compound 4.[a]



[a]In this scheme, the intermediates with the μ-η^5 cycloheptatrienyl units are meant to represent η^2-Rh; η^3-Ru and η^4-Rh; η^1-Ru bonding modes.

The final *CO enriched product does contain the original η^4-Rh; η^3-Ru bonding mode. It is drawn as shown to indicate the non-discriminate nature of the *CO enrichment process.

equilibrium between $\mu-\eta^7$ and $\mu-\eta^5$ ring species of the starting material, followed by ^{13}CO attack of the coordinatively unsaturated $\mu-\eta^5$ species, or by a one-step associative ^{13}CO addition. Similar mechanisms involving hapticity changes have been used to explain the enhanced rate of carbonyl substitution in η^5-indenyl and η^5-fluorenyl type complexes.[36] Thus the carbonyl exchange process is accelerated by stabilization of the transition state.

In view of these results it seemed worthwhile to study the phosphine substitution reactions of the penta-carbonyl **4** in order to compare the results with previously established trends.[30]

B. Reaction of **4** with Triphenylphosphine

The reaction between triphenylphosphine and compound **4** is very fast. The reaction with one equivalent of triphenylphosphine occurs readily in hexane at room temperature and the phosphine substituted derivative **5** precipitates as a red solid in a few minutes, eq. 8

$$\underset{\mathbf{4}}{(\mu\text{-}C_7H_7)RuRh(CO)_5} + PPh_3 \xrightarrow[r.t]{\text{hexane}} \underset{\mathbf{5}}{(\mu\text{-}C_7H_7)RuRh(CO)_4PPh_3} + CO \qquad (8)$$

The infrared spectrum of the product shows four bands in the carbonyl region at 2009(s), 1982(s), 1941(s), and 1809(m,br) cm^{-1}, indicating both terminal and bridging carbonyl moieties. The doublet feature in the $^{31}P\{^{1}H\}$ NMR spectrum at 40.88 ppm, due to coupling between phosphorous and ^{103}Rh (J_{Rh-P} = 183.3 Hz), clearly establishes that substitution of triphenylphosphine occurs on the rhodium centre. The nucleophilic attack on rhodium is not surprising since Rh(I) is known to form many $16e^-$ species[37] and therefore is prone to accommodate coordinative unsaturation favourable to initiate phosphine substitution. Similar substitutional preference was also seen with $(\mu\text{-}C_7H_7)Fe(CO)_3Rh(CO)_2$.[30]

Simple electron counting reveals that the formation of the bridging carbonyl moiety must be accompanied by a reversal of the bonding mode between the bridging cycloheptatrienyl ligand and the ruthenium and rhodium framework. This is accomplished by a change in the bonding mode of the C_7H_7 moiety from η^3-Ru, η^4-Rh in **4** to η^3-Rh and η^4-Ru in **5**. This type of bonding was observed earlier for $(\mu\text{-}C_7H_7)(\mu\text{-}CO)Fe(CO)_2Rh(PPh_3)(CO)$ and was confirmed by X-ray crystal structure determination of $(\mu\text{-}C_7H_7)(\mu\text{-}CO)Fe(CO)_2Rh(DPPE)$ (DPPE = bis(diphenylphosphino)ethane).[30]

The proton NMR spectrum of the compound is simple and

shows a sharp singlet for the C_7H_7 ring at 3.9 ppm and phenyl protons around 7.4 ppm.

Figure 6 shows the variable temperature ^{13}C NMR spectra in the carbonyl region. At room temperature, only a single broad peak is seen. As the temperature is lowered, the resonance splits into two peaks, thereby indicating that the unique signal at room temperature must be the result of rapid intermetallic carbonyl group exchange and is not due to accidental overlap of the carbonyl signals. The high field resonance is a doublet of doublets, clearly assignable to the carbonyl group on rhodium split by coupling to both ^{103}Rh and ^{31}P. However the observation of a low field signal of relative intensity of three is not consistent with the ground state structure deduced from infrared spectroscopy which showed a bridging carbonyl moiety. The single resonance must arise from rapid scrambling between bridging and terminal carbonyl groups localized on the ruthenium atom. Attempts to freeze out the low temperature limiting spectrum met with failure. The resonance broadened noticeably but remained a single peak even at -90°C. The most plausible explanation for the carbonyl group scrambling on ruthenium is a one-for-one bridge opening and closing mechanism which can be subdivided into (i) synchronous one-for-one bridge-terminal group exchange and (ii) a stepwise process

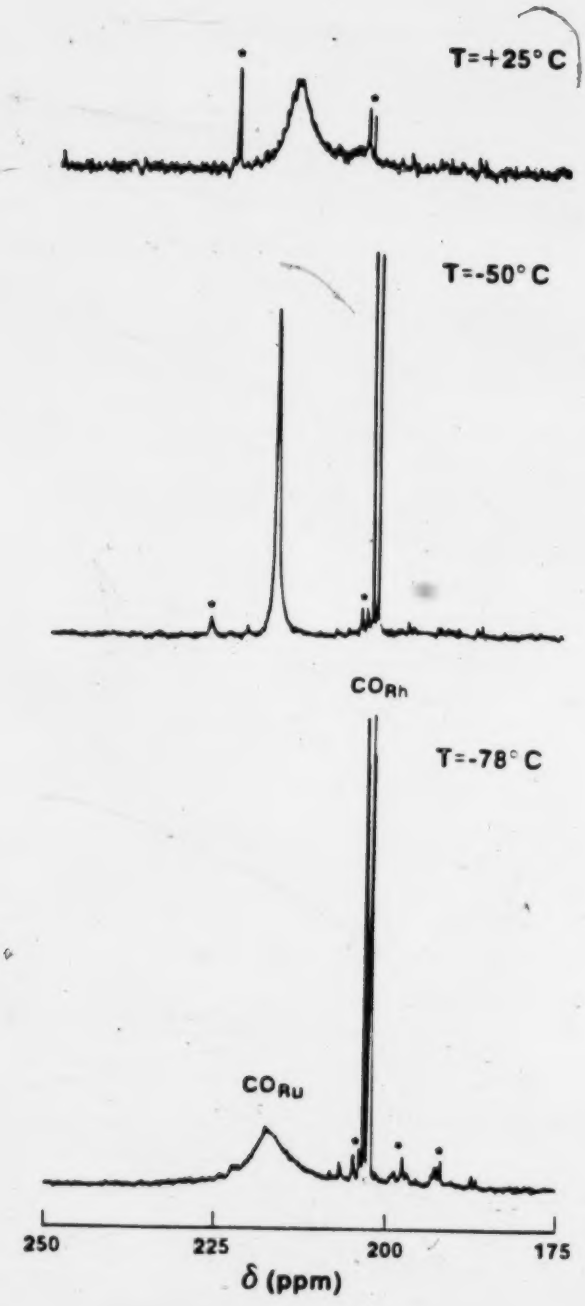
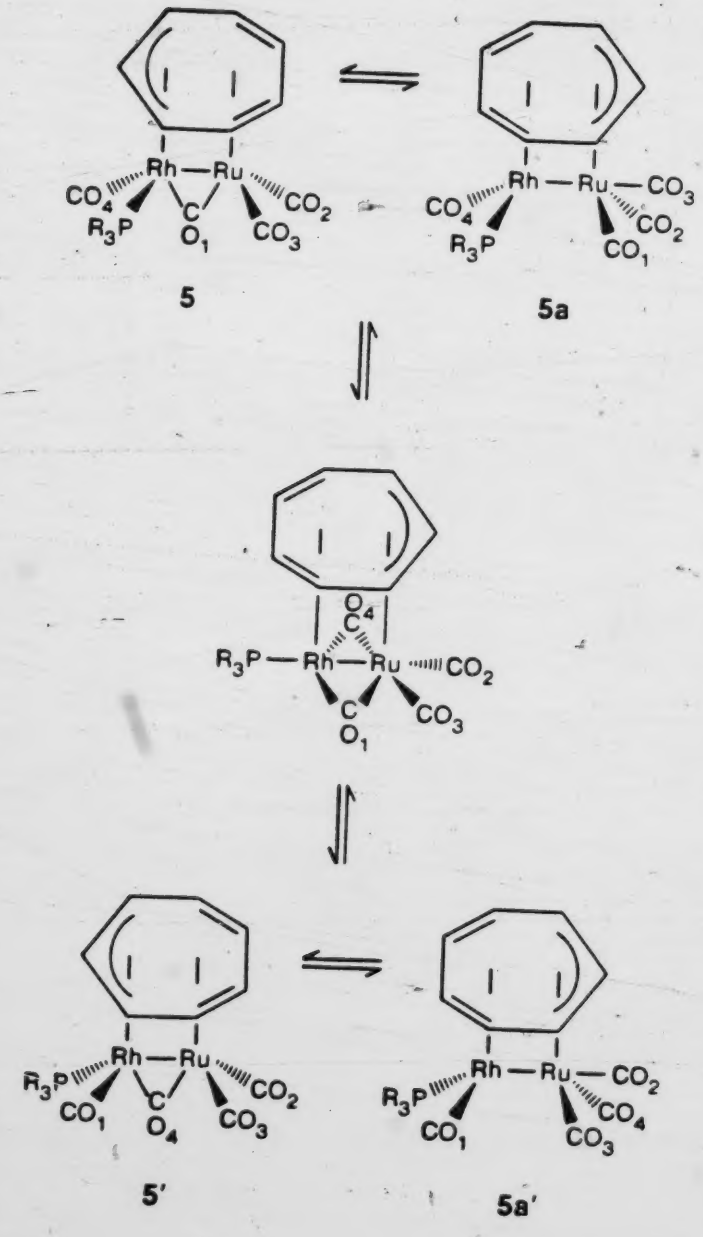


Figure 6. Variable Temperature ^{13}C NMR Spectra of $(\mu\text{-}C_7H_7)RuRh(CO)_4PPh_3$, 5. *Impurities.

via an unbridged form. The former process was favoured to explain the fluxional behaviour of $Cp_2Rh_2(CO)_2L$ (L = $P(Oh_3)_3$, PMe_2Ph, CO)[38] compounds which contain one bridging CO moiety, while the latter process was invoked for the CO scrambling in $Cp_2Fe_2(CO)_4$[39] and similar types of molecules containing two bridging carbonyl groups. We favour this latter process in the present context even though complex **5** possesses only one bridging carbonyl group. The reason is that, as shown in Scheme 4, the fluxionality of the C_7H_7 ring aids the movement of the bridging carbonyl group into the terminal position thereby stabilizing the putative "all terminal" intermediate[5a] in the scrambling process.

Also shown in the scheme is a plausible reaction pathway for global carbonyl scrambling in the complex. Although other intermediates can be envisaged, the doubly bridged form shown is favoured since it is accessible from both the ground state and the isomeric "all terminal" formulation for **5**. The free energy of activation obtained for intermetallic carbonyl group movement at 20°C is 11.0 kcal/mol which is lower than in the parent pentacarbonyl **4**. This follows the normal trend of more facile for carbonyl group scrambling in bi- and polynuclear metal carbonyls following phosphine substitution.[34,40]

Scheme 4. Local (Ru) and Intermetallic CO Exchange in 5.



C. Reaction of 4 with Bis(diphenylphosphino)methane ($Ph_2PCH_2PPh_2$, DPPM)

1. Synthesis and Characterization of $(\mu\text{-}C_7H_7)RuRh(CO)_3DPPM$

Bimetallic compounds containing the ditertiary phosphine, bis(diphenylphosphino)methane, are being increasingly synthesized and their interesting chemistry explored. The ligand is known to exhibit monodentate or chelating and bridging bidentate behaviour towards transition metals. Although complexes with chelating DPPM are known, the four membered ring so formed is strained and in bimetallic compounds the ligand has a greater tendency to act as a bridging bidentate unit between the two metal atoms.[41] Indeed the reaction of the Fe-Rh pentacarbonyl with DPPM gave initially the DPPM chelated complex, $(\mu\text{-}C_7H_7)(\mu\text{-}CO)Fe(CO)_2Rh(DPPM)$, which precipitated from hexane solution. However in solution (benzene, methylene chloride) the compound smoothly isomerized to the bridging DPPM form.[30]

The reaction of the pentacarbonyl **4** with one equivalent of DPPM readily forms a deep red solid which precipitates from hexane solution, eq. 9. Elemental analysis and mass spectrum are consistent with the formulation $RuRh(C_7H_7)DPPM(CO)_3$, **6**.

$$(\mu\text{-}C_7H_7)RhRu(CO)_5 + 1\ DPPM \rightarrow (\mu\text{-}C_7H_7)RhRu(CO)_3DPPM + 2CO \quad (9)$$
4 6

The infrared spectrum of this compound has three bands in the terminal carbonyl region (1975(s), 1940(s), and 1904(br) cm^{-1}. This result was quite interesting and unexpected since as stated above, the reaction of $(\mu\text{-}C_7H_7)Fe(CO)_3Rh(CO)_2$ under similar experimental conditions gave the chelating compound $(\mu\text{-}C_7H_7)(\mu\text{-}CO)Fe(CO)_2Rh(DPPM)$, which also contains a bridging carbonyl moiety. The synthesis was repeated at low temperature in an attempt to intercept the elusive chelating DPPM isomer. The reaction was slow to begin with, but again the material which precipitated from the hydrocarbon solvent had the same IR features as above.

The proton decoupled ^{31}P NMR spectrum of the compound at room temperature shows a six-line spectrum which exhibits little temperature dependence except for further small splitting of the two low field lines, Figure 7. Consistent with the bridged DPPM formulation, the phosphorous nuclei are inequivalent. However the observed chemical shifts are small and comparable to the strong coupling between the two phosphorous nuclei, thus giving rise to the AB part of an ABX spin system, with ^{103}Rh being the X component. The phosphorous atom (B), attached

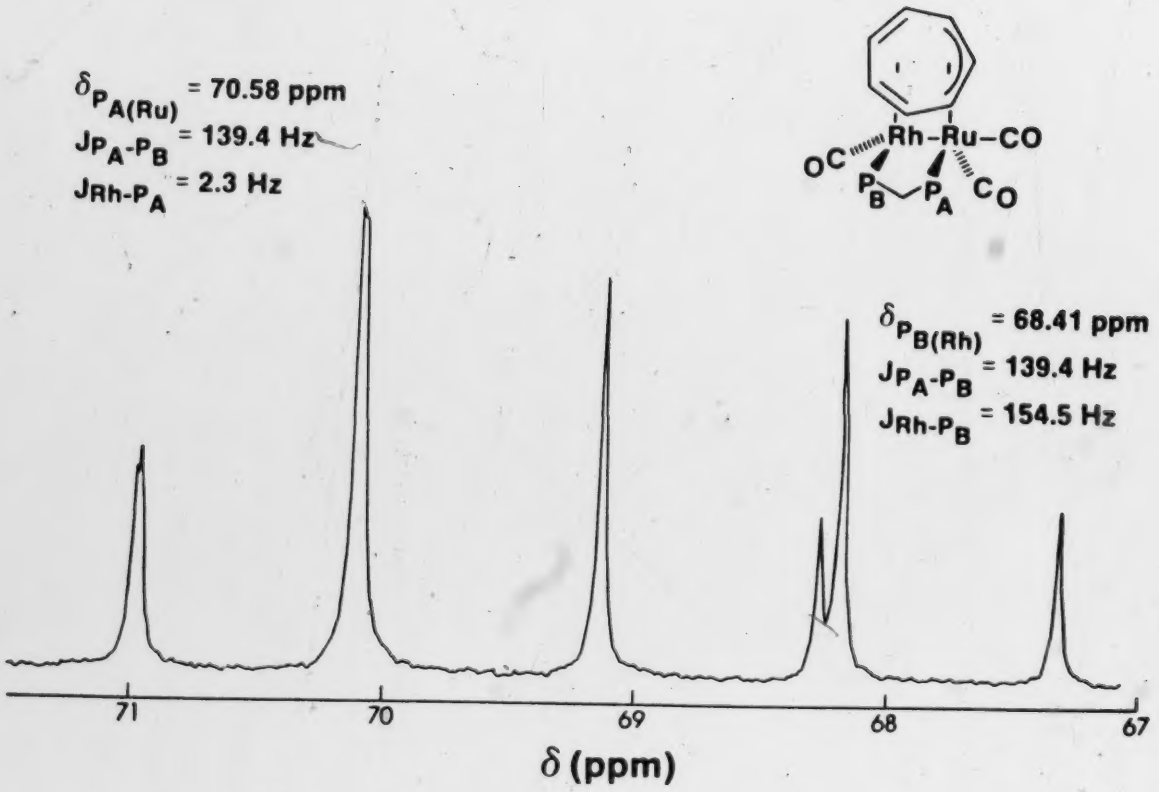


Figure 7. $^{31}P\{^1H\}$ NMR Spectrum of $(\mu\text{-}C_7H_7)RuRh(CO)_3DPPM$, 6.

to rhodium, is also strongly coupled to ^{103}Rh which further splits the B branch and gives rise to the four high field lines. Small, long range, coupling to rhodium of the ruthenium bound phosphorous P_A is responsible for the doublet appearance of the low field lines. Analysis of the spectrum gave the chemical shift and coupling constant values shown in Figure 7.

The low temperature proton NMR of the compound shows a broad singlet at 3.9 ppm for the C_7H_7 ring, resolved multiplets for the methylene protons at 1.95 and 4.05 ppm, while the phenyl protons are seen between 7.2 and 7.4 ppm, also in accord with the formulation.

The ^{13}C spectrum, Figure 8, at low temperature shows a broad single line for C_7H_7 ring and in the carbonyl region a doublet of doublets at 201.7 ppm and two lines at 209.6 and 199.8 in the ratio of 1:1:1. The intermediate field signal (d,d) is clearly the carbonyl group on rhodium split by coupling to both ^{103}Rh and ^{31}P (J_{Rh-C} = 76.7 Hz, J_{P-C} = 12 Hz). The other two signals are due to the carbonyls on ruthenium. Small, long range, coupling to phosphorous is responsible for the further splitting of one of the lines (J = 7.0 Hz). This spectrum is consistent with the ground state structure of the compound. However, as the temperature is raised, the lines due to carbonyls on ruthenium broaden and coalesce

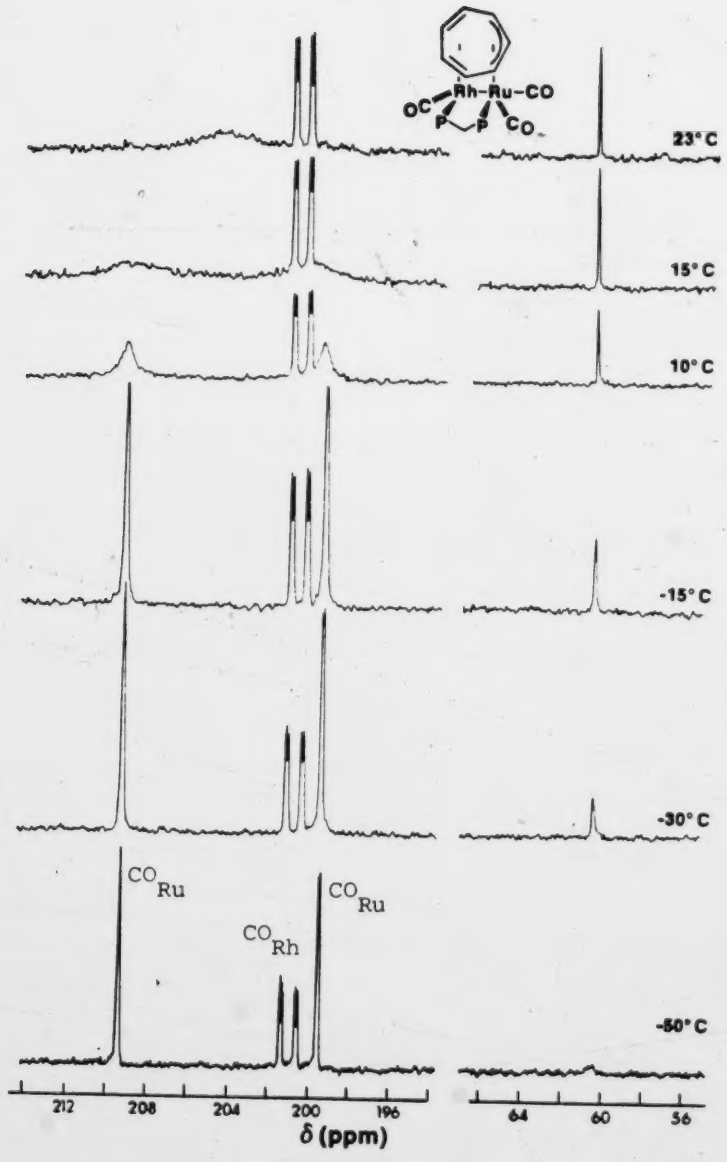


Figure 8. Variable Temperature ^{13}C NMR Spectra of $(\mu\text{-}C_7H_7)(\mu\text{-DPPM})Ru(CO)_2Rh(CO)$, 6 ($CD_2Cl_2$).

at approximately 0°C and at room temperature appear as a broad signal. In order to observe the high temperature limiting spectrum, the spectrum was recorded in toluene-d_8, Figure 9. The emergence of a single sharp line at 60°C indicates fast exchange of the carbonyls on ruthenium. Free energy of activation for carbonyl scrambling on ruthenium is 12.6 kcal/mol at 20°C.

Although localized carbonyl group scrambling on metal centres is by now a well established phenomenon and has been observed in all compounds synthesized in this work, its relatively ready occurrence in the presence of the bridging DPPM ligand of complex **6** was surprising. Since the exchange of the two carbonyl moieties on ruthenium must involve some angle bending of the ligating groups, including the coordinated phosphine as well, in the present context this demands tandem movement of the two phosphorous nuclei of DPPM ligand and consequently rearrangement of both metal centres. A plausible scenario for the exchange mechanism is shown in Scheme 5. The proposal takes into account the coordination geometry of the respective metal centres and the commonly observed rearrangement processes at such sites. As shown in the scheme, in its ground state compound **6** contains a five coordinate square pyramidal rhodium atom and a six coordinate octahedral ruthenium centre if a formal two

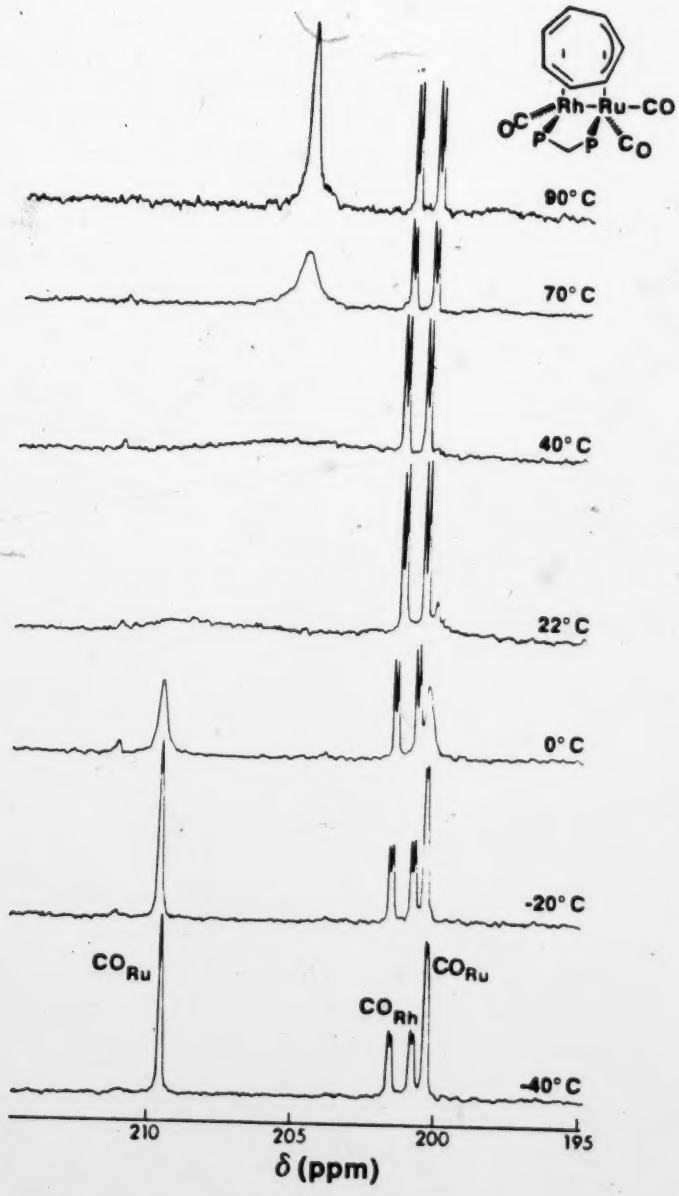
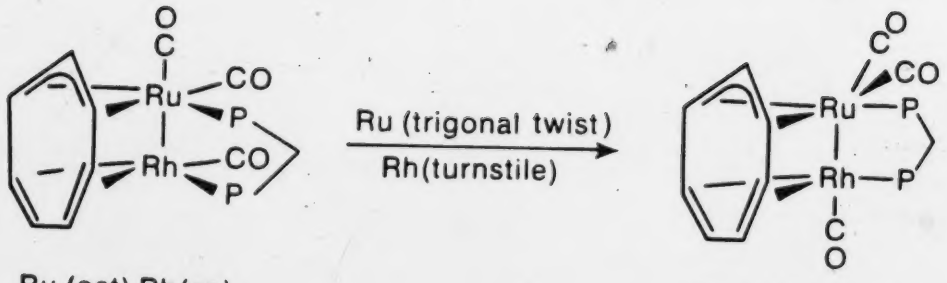


Figure 9. Variable Temperature ^{13}C NMR Spectra of $(\mu\text{-}C_7H_7)(\mu\text{-DPPM})Ru(CO)_2Rh(CO)$, 6 (Toluene-$d_8$).

Scheme 5. CO Scrambling on Ruthenium in Compound 6.



Ru (oct) Rh(sp)

Ru(tp) Rh (tbp)

coordination position is assigned to the η^3-allyl fragment. The proposed rearrangement thus involves the well known square pyramidial-trigonal bipyramidal motion at Rh and the typically higher energy trigonal twist type process at ruthenium which results in a change of coordination geometry from octahedral to trigonal prismatic. It is clear from the scheme that the high energy intermediate has a symmetry plane passing through the ruthenium and rhodium atoms and comprises the DPPM ligand. The mirror plane renders the two carbonyl groups on ruthenium equivalent. Although not completely conclusive, strong support for the proposed pathway for carbonyl group scrambling comes from the temperature dependent behaviour of the methylenic proton signals. The two multiplets seen at low temperature broaden as the temperature is raised and coalesce around 20°C. The free energy of activation for methylene proton exchange is 12.4 kcal/mol, virtually the same as that seen for carbonyl group scrambling on ruthenium.

2. ^{31}P NMR Studies of the Reaction of Compound **4** with DPPM

The reaction between the pentacarbonyl **4** and DPPM as described earlier, results in the formation of bridged DPPM compound. The same product is obtained even at low temperature. Since the reaction between DPPM and

$(\mu\text{-}C_7H_7)Fe(CO)_3Rh(CO)_2$ gave the rhodium chelated DPPM derivative as the initial kinetic product, it was of interest to follow the reaction of **4** with DPPM by ^{31}P NMR spectroscopy in order to identify elusive intermediates and thereby elucidate the mechanism of formation of **6**.

a. Initial experiment

The proton decoupled ^{31}P NMR spectra, $^{31}P\{^1H\}$, recorded at different temperatures and reaction times are shown in Figure 10 and the NMR data are given in Table 4.

The spectrum recorded soon after the reagents were mixed at -50°C shows two signals at 44.4 and -25.7 ppm, quite distinct from the ^{31}P NMR features of compound **6**. No resonance is seen at the position of free DPPM at -23 ppm, indicating complete consumption of **4** and DPPM. The observation of two ^{31}P signals shows that the intermediate formed at this stage of the reaction contains two different types of phosphorous nuclei. The resonance at -25.7 ppm is in the region of uncoordinated DPPM ligand, its doublet appearance is due to coupling to the other chemically different phosphorous atom. The doublet of doublets at 44.4 ppm is clearly due to a phosphorous nucleus coupled to both ^{103}Rh and ^{31}P. This information identifies the intermediate (designated as **5A** in the figure) as containing a monodentate DPPM ligand bound to rhodium. This result is not surprising since it is

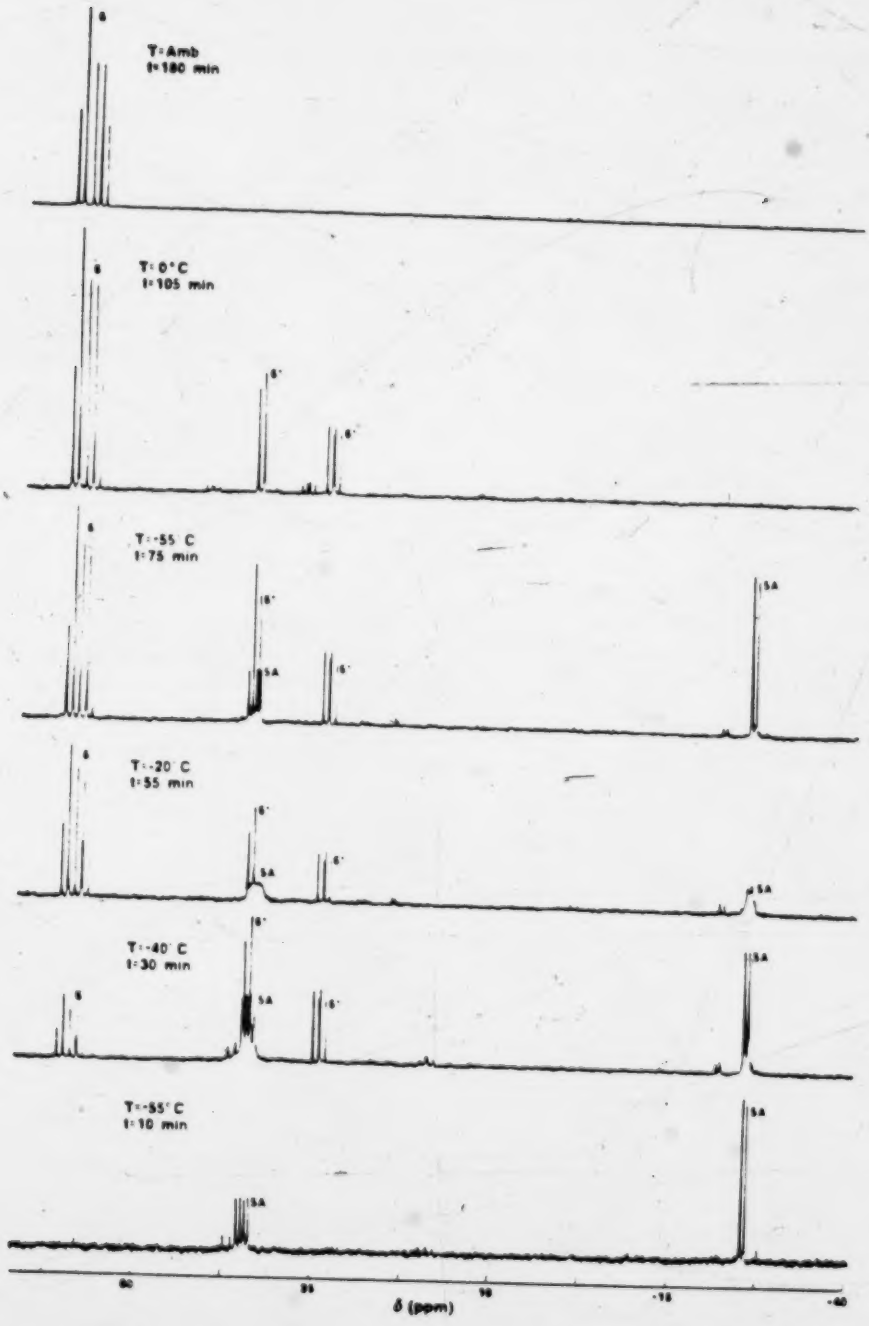


Figure 10. ^{31}P NMR Study of the Reaction of $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2$ with DPPM (Initial Temperature, -55°C).

Table 4. $^{31}P\{^{1}H\}$ NMR Data for the Intermediates Identified in the Reaction of Compound **4** with DPPM.

Species	Atom[a]	Multiplicity[b]	δ (ppm)	J (Hz) J_{P-P}	J (Hz) J_{Rh-P}
5A	P	d	-25.7	96.0	-
	P_{Rh}	dd	44.4	96.0	178.6
6*	P_{Ru}	d	44.2	127.0	-
	P_{Rh}	dd	33.6	127.0	151.6
6**	P_{Ru}	m	22.5		
	P_{Rh}	m	10.1		
6‡**	P_{Ru}	m	21.25		
	P_{Rh}	m	9.25		
7	$P_{Rh}P_{Rh}$	d	-22.1		97.9

[a] P = uncoordinated phosphorous.

[b] d = doublet, dd = doublet of doublets, m = multiplets.

consistent with the initial site of attack observed in the reaction of **4** with one equivalent of PPh_3 giving **5**.

Warming the sample to -40°C results in a spectrum (t = 30 min) which still shows the presence of η^1-DPPM intermediate. The six line ABX pattern at around 70 ppm heralds the formation of the final bridging DPPM, complex **6**. However the appearance of additional signals at 34 and 44 ppm indicate that the conversion of **4** to **6** is not a simple one step process but occurs via the intermediacy of at least one more step. Interestingly this other intermediate is not the Rh chelated DPPM complex akin to the kinetic product in the Fe-Rh reaction referred to before. Indeed such a molecule would have equivalent phosphorous nuclei and is expected to show a simple doublet in the ^{31}P NMR spectrum. Contrary to this the intermediate observed presently must have two distinct phosphorous nuclei, one bonded to rhodium (doublet of doublets at 33.6 ppm) and the other to the ruthenium (simple doublet at 44.2 ppm). Therefore this is another DPPM bridged Ru-Rh complex, similar, yet different from the final product **6** (designated **6*** in the figure). Further warming of the sample to -20°C (t = 55 min) results in no new signals but causes broadening of the signals assigned to the η^1-DPPM intermediate. Since line shape changes are indications of reversible chemical

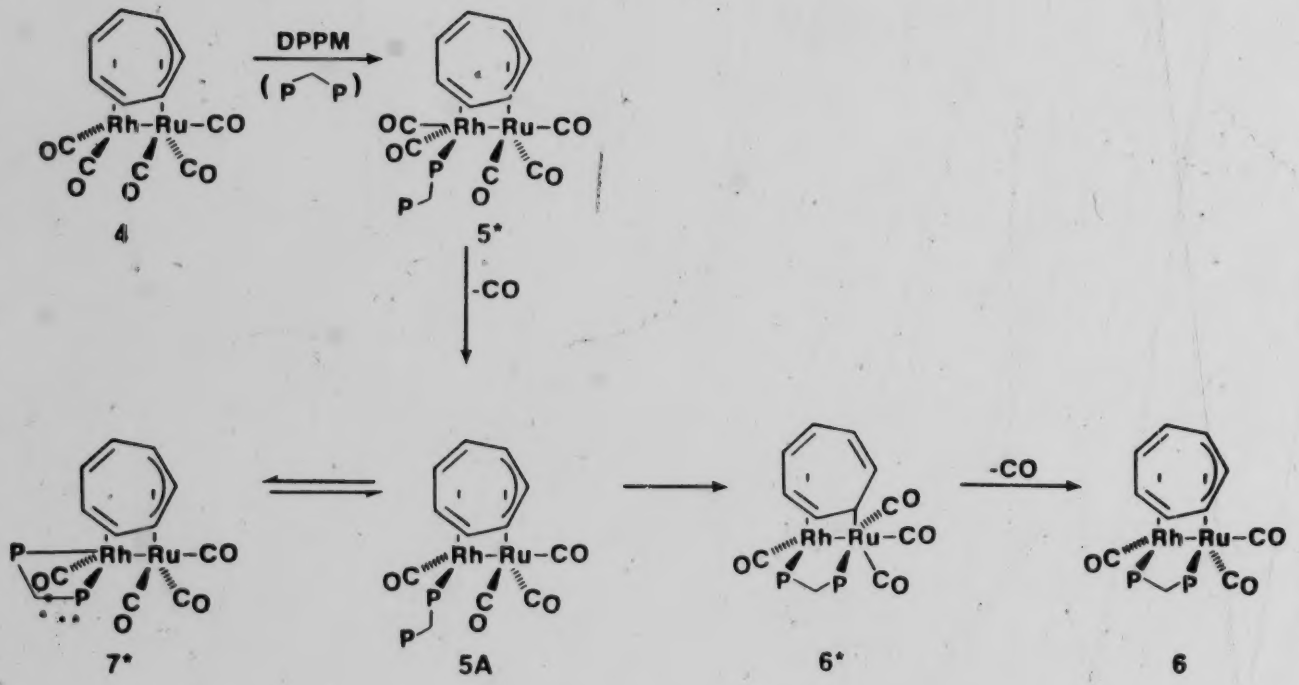
exchange processes. The temperature was immediately quenched back to -55°C and the spectrum recorded at this temperature (t = 75 min). The reemergence of sharp η^1-DPPM signals serve to verify the postulate and gave indication that at -20°C there is some exchange process that begins to equilibrate the environments of the two ends of the η^1-DPPM ligand.

Raising the temperature to ambient results in the disappearance of η^1-DPPM, and the signals due to **6*** and **6** increase in intensity. Finally **6*** is seen to convert completely to **6**.

Based on these observations the reaction pathway shown in Scheme 6 is proposed for the formation of **6** from **4** and DPPM.

The first step in the reaction is clearly an attack of the DPPM ligand at the rhodium centre. This most probably occurs without loss of CO in a bimolecular associative step. The coordinative unsaturation being provided by the flexible μ-C_7H_7 moiety changing its bonding mode from μ-η^7 to μ-η^5. Carbon monoxide loss then results in a complex (**5A**) related to the PPh_3 substituted compound **5**, where a dangling η^1-DPPM ligand fulfills the role of the phosphine moiety. Presently, in the absence of ^{13}C NMR data we cannot unequivocally identify the ^{31}P observed η^1-DPPM intermediate as **5*** or **5A**, although we

Scheme 6. Proposed Mechanism for the Formation of 6 From 4 and DPPM.



favour the latter.

No such ambiguity exists concerning the nature of the next intermediate. Even in the absence of ^{13}C NMR data it is clear that in order to produce a complex containing a bridging DPPM ligand which is distinct from **6**, the unsaturation needed at ruthenium must be provided by the bridging cycloheptatrienyl ligand. Intramolecular attack by the free phosphorous atom of the dangling DPPM ligand on ruthenium thus proceeds by displacement of a double bond of the μ-C_7H_7 moiety, without CO loss, to give **6***. The latter at -40°C slowly (more rapidly at high temperatures) loses CO to give **6**. It is interesting to note that the exchange of environment of the two ends of the η^1-DPPM moiety in **5A**, as seen by line broadening at -20°C, provides evidence for cycloheptatrienyl double bond dissociation at the Rh centre, equilibrium between **7*** and **5A** in the scheme. These findings represent the first conclusive demonstration of the flexible bonding capability of the μ-C_7H_7 moiety and of the postulated "incipient coordinative unsaturation" provided by the ligand.

b. Later findings

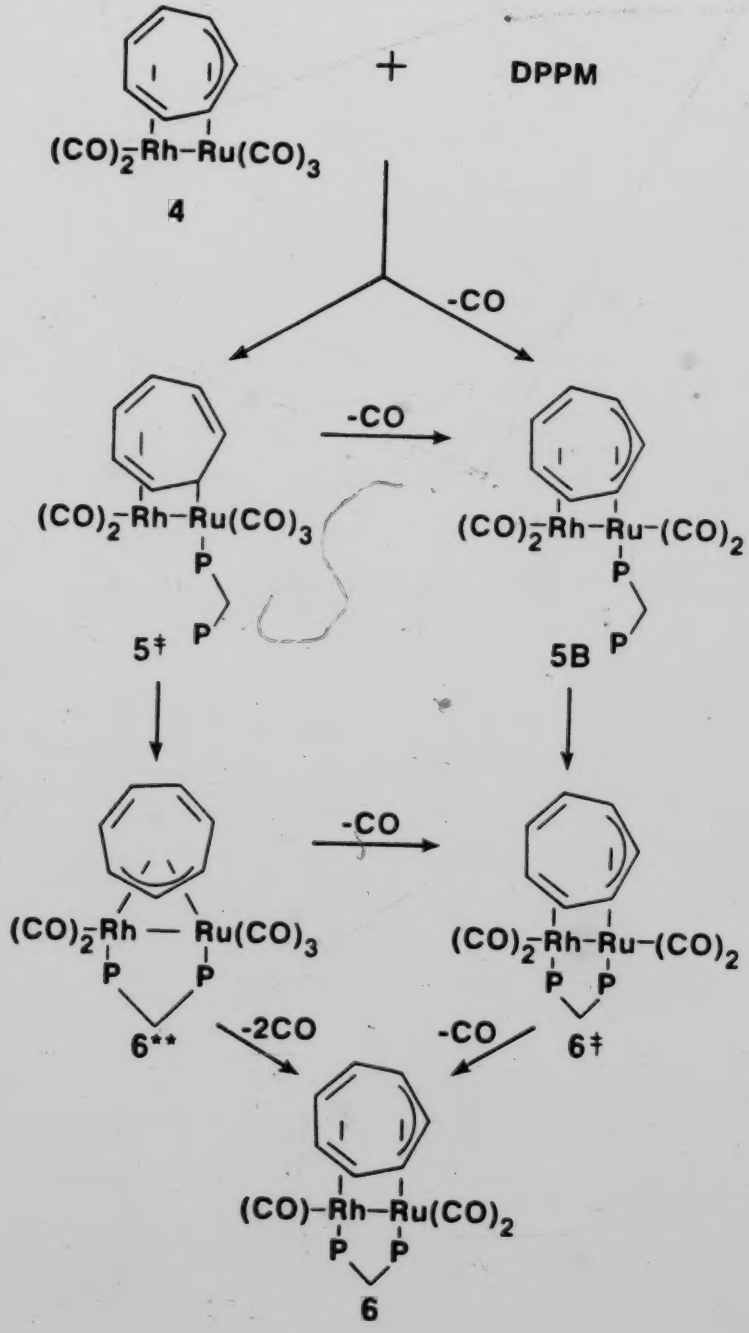
In order to observe initial ^{31}P NMR spectrum which still contained free DPPM ligand, the NMR studies were reinvestigated by mixing the reagents and recording the

initial NMR spectrum at -80°C instead of -50°C. In fact free DPPM was seen, however, several new resonance lines, in addition to those due to the previously observed intermediates appeared. As the temperature was raised the intensities of the new signals changed but ultimately converted to the DPPM bridged product **6**. This led us to consider that at low temperature a competitive reaction, involving attack of DPPM on the ruthenium centre was also occurring. Scheme 7 details the plausible intermediates from such an initial step and the pathway for conversion to complex **6**.

Following the above observations, several ^{31}P NMR studies were initiated at -80°C to follow the reaction of pentacarbonyl **4** with DPPM. Due to the many possible intermediates involved the spectra were complicated and the intensities of the individual components seemed to depend mostly on the amount of starting material used and time of mixing. Only a few representative spectra, which most clearly show the formation of the new intermediates, are shown in Figure 11 with approximate time of reaction.

The initial spectrum was recorded at -80°C, immediately after mixing the reagents at this temperature, showed free DPPM and the previously seen rhodium bound η^1-DPPM intermediate **5A**. However consumption of free DPPM at this temperature did not give **6*** and **6** cleanly, instead

Scheme 7. Formation of 6 From 4 and DPPM via Initial Ru Attack.



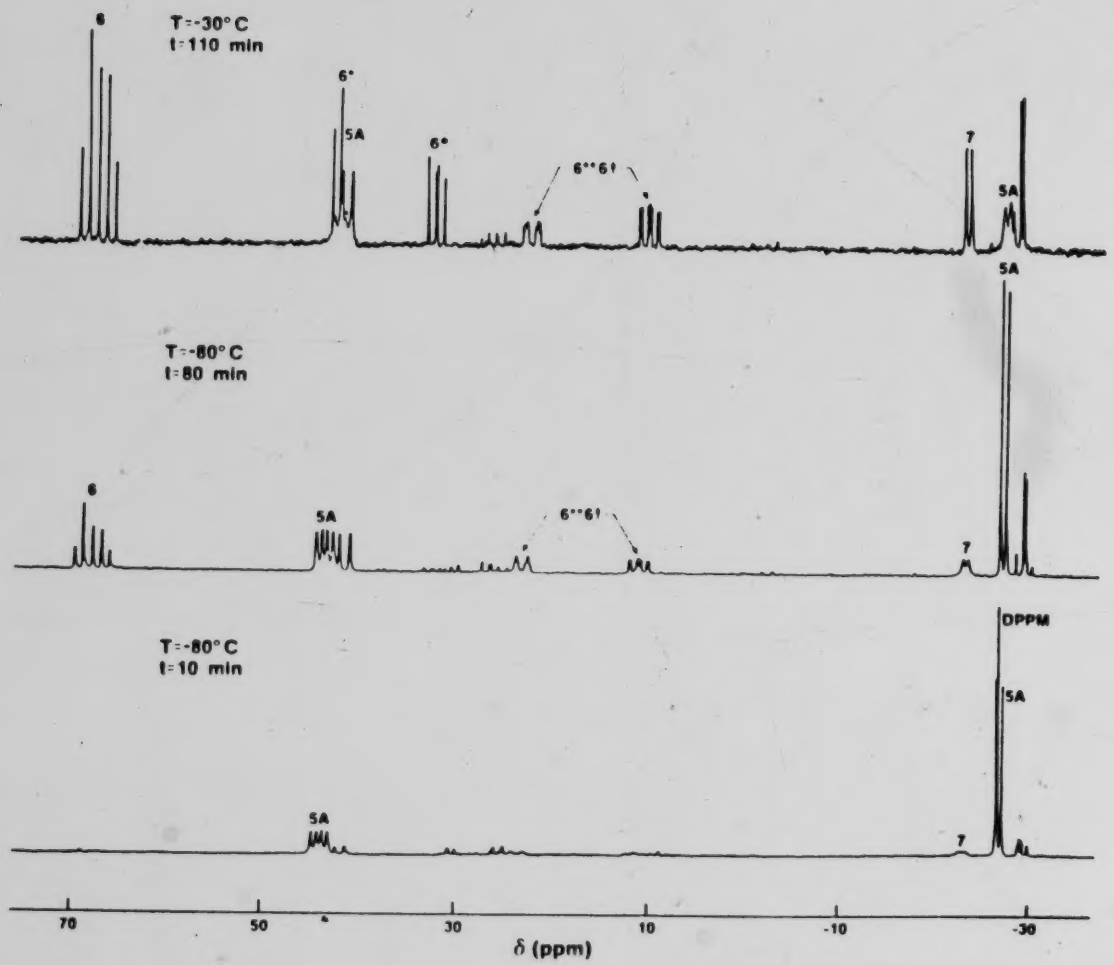


Figure 11. ^{31}P NMR Study of the Reaction of $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2$ with DPPM (Initial Temperature, -80°C).

new signals were observed in the spectra. After 80 minutes at -80°C, and even better defined in the t = 110 min and T = -30° spectrum, three sets of doublets at -28.1 ppm (J = 46.9 Hz), -22.1 ppm (J = 97.9 Hz), 43.5 ppm (J = 169.4 Hz) and two multiplets at 10.1 and 22.5 ppm were also seen. The position and multiplicities of the last resonances are most consistent with some DPPM bridged species and accordingly they are tentatively identified as **6**** and **6‡**. The observation of new doublets in the free DPPM region looked promising for the putative ruthenium bound η^1-DPPM intermediates, **5B** and/or **5‡**. However such an intermediate would be expected to have two doublets with identical spacings due to coupling between the two different phosphorous nuclei of the η^1-DPPM ligand. Yet all three doublets show different line separations, implying that these resonances belong to different chemical species. Careful search of the obtained spectra could not reveal the needed partner doublet of **5B**/**5‡**. Indeed the nature of the species giving rise to the three doublets remains an enigma. One of the doublets could be due to the elusive rhodium chelated DPPM complex, $(\mu\text{-}C_7H_7)(\mu\text{-}CO)Ru(CO)_2Rh(DPPM)$ **7**. The analogous Fe-Rh complex exhibits a doublet at -13.44 ppm (J_{Rh-P} = 152.3 Hz) and on this basis we tentatively formulate the doublet at -22.1 ppm as belonging to **7**. We have no explanation as

to why this compound appears to form only when the reaction is initiated at very low temperature, nor can we offer reasonable formulation for the remaining two doublets.

Thus, although plausible, initial ruthenium attack of compound **4** by DPPM as detailed in Scheme 7 remains unproven.

D. Conclusions

The reaction of pentacarbonyl **4** towards phosphine is facile and results in mono- (PPh_3) and disubstituted (DPPM) complexes in virtually quantitative yield. The reaction with DPPM proved interesting. The formation of product **6** is not a single step process, but proceeds via a multistep pathway. Low temperature ^{31}P NMR studies have revealed competitive initial Rh and Ru attack by DPPM. The reaction is associative in nature and the different bonding capabilities of the cycloheptatrienyl moiety is definitely responsible for the observed scenerio. A complimentary low temperature ^{13}C NMR study is clearly warranted in order to corroborate some of the proposed intermediates and to resolve the remaining ambiguities. It will be of interest to explore the reactivity of compound **6** towards protonation and alkylation reactions.

CHAPTER 5

EXPERIMENTAL SECTION

A. Solvents and General Techniques

All experimental procedures were performed in standard Schlenk vessels under a static atmosphere of vigorously purified nitrogen or argon. This was accomplished by passing the commercial gases through a heated column (90-100°C) containing BASF Cu-based catalyst (R3-11) to remove oxygen and a column of Mallinkrodt Aquasorb, which is P_2O_5 on an inert base, to remove water.

All glassware was heated in an oven to 100-120°C and then immediately evacuated and filled with the inert gas prior to any operation.

Solvents were dried by refluxing under nitrogen with the appropriate drying agent, Table 5, and distilled just prior to use. When needed, solvents were degassed before use by repeated freeze-pump-thaw cycles. Pentane and hexane were preconditioned before being refluxed and distilled by stirring over concentrated H_2SO_4, until no colour developed in the acid layer, washed with water and dried over Na_2SO_4.

Table 5. Drying Agents Used for Solvents.

Solvent	Drying Agent
1. Pentane	Calcium hydride
2. Hexane	Potassium metal
3. Benzene	Potassium metal
4. Toluene	Sodium metal
5. Diethylether	Sodium-potassium alloy/benzophenone
6. Tetrahydrofuran	Potassium/benzophenone
7. Dichloromethane	Phosphorous pentoxide

B. Starting Materials and Reagents

Dodecacarbonyltriruthenium[42a,b] and $[Rh(COD)Cl]_2$[43] were prepared by standard literature methods. Hydrated rhodium trichloride was a loan from Johnson Matthey Inc. Diphenylphosphinomethane was obtained from Pressure Chemical Company, ^{13}CO from Monsanto Research Corporation and triphenylphosphine, cycloheptatriene, and KO^tBu were purchased from Aldrich Chemical Co. KO^tBu was sublimed and cycloheptatriene was distilled before use.

C. Physical Measurements

Infrared spectra were obtained with a Nicolet MX-1 Fourier transform interferometer. Abbreviations used in reporting the spectra: s strong; s,br strong broad; m medium; w weak; and sh shoulder.

NMR spectra were recorded on a Bruker WP-200 or Bruker WP-400 spectrometer. Variable temperature NMR studies were carried out with sample tubes sealed under vacuum. Chemical shifts, δ ppm, are reported relative to TMS (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P). Abbreviations to indicate multiplicities are: s singlet; d doublet; dd doublet of doublets; t triplet; q quartet; and m multiplet.

Free energies of activation at coalescence temperature, $\Delta G^{\ddagger}_{Tc}$, were calculated using the expression:[32]

$$\Delta G^{\ddagger} = 4.57\ Tc\ [9.97 + \log\ [\frac{Tc}{\Delta \nu}]$$

Tc = coalescence temperature °K

$\Delta \nu$ = chemical shift difference in Hz

$\Delta G^{\ddagger}$ = kcal/mole

D. Procedures, Chapter 2

Preparation of (η^4-cycloheptatriene)tricarbonylruthenium, (η^4-C_7H_8)$Ru(CO)_3$, 1

Dodecacarbonyltriruthenium (2 g, 3.13 mmol), cycloheptatriene (20 mL, d = 0.88 g/mL) and benzene (300 mL) were placed in a 500 mL elongated (15 cm length and 7 cm diameter) reaction flask under argon. The reaction vessel was fitted with a water-cooled condenser. The light source, a 450 W high pressure Hanovia mercury lamp, was placed in a water-cooled quartz immersion well. The distance between the light source and the reaction flask was approximately 7 cm. As the reaction proceeded upon irradiation, the temperature of the mixture raised to ~70°C and the solid $Ru_3(CO)_{12}$ dissolved completely. Irradiation for 24 hours was necessary for the complete consumption of the starting material. After the reaction was complete, the benzene was stripped off under vacuum and the residue was extracted with 50 mL of pentane. The filtered extract was concentrated to 5-10 mL and was then placed on a chromatography column (10 cm × 3 cm) packed with silica gel (Merck, Kieselgel 60, 230-400 mesh). Elution with hexane caused the development of a pale yellow band. This first band, eluted with 50 mL of hexane, was discarded as it mainly contained impurities;

Ditropyl, $Ru(CO)_3(C_7H_{10})$ and $Ru_2(CO)_6(C_7H_8)$. A second yellow band moved down the column upon further elution with hexane. This band was collected (500 mL) in a one-necked flask under argon. The solution was concentrated to ~5 mL and cooled to -78°C for several hours to cause precipitation of the dinuclear compound, $Ru_2(CO)_6(C_7H_8)$. The clear supernatant yellow solution was carefully inverse filtered into another one-necked flask. Removal of the solvent under vacuum gave $Ru(CO)_3(C_7H_8)$ as a pale yellow oil (2.2 g, 84.6%). At this stage of the chromatographic separation the trinuclear ruthenium cluster compound, $Ru_3(CO)_6(C_7H_7)(C_7H_9)$, stays on top of the chromatography column. If desired, it can be eluted with methylene chloride.

To obtain an analytically pure sample of $Ru(CO)_3(C_7H_8)$, the pale yellow oil was chromatographed twice on a short column of silica gel (5 cm × 3 cm). The combined hexane eluants (2 × 200 mL) were concentrated to 5 mL and were cooled to -78°C. The supernatant solution was transferred to a small Schlenk tube and the solvent was removed under vacuum to give a clear pale yellow oil (1.7 g, 65.3%). Elemental analysis; Anal. calcd. for $C_{10}H_8O_3Ru$: C 43.32; H 2.89. Found; C 43.81; H 3.08. IR (hexane): ν_{CO} 2066(s), 2002(s), and 1991(s) cm^{-1}. NMR data are shown in Table 1 of Chapter 2.

Preparation of potassium (η^3-cycloheptatrienyl)tricarbonylruthenate(-1), $K(\eta^3\text{-}C_7H_7)Ru(CO)_3$, 2

A typical procedure is as follows: 700 mg of (η^4-C_7H_8)$Ru(CO)_3$ (2.53 mmol) was dissolved in 30 mL of dry and deoxygenated THF under argon. The solution was kept at -78°C in dry ice. Freshly sublimed KO^tBu (284 mg, 2.53 mmol) was dissolved in 50 mL of THF at room temperature. The clear THF solution of KO^tBu was added slowly via a canula to the cold, magnetically stirred solution of (η^4-C_7H_8)$Ru(CO)_3$. The addition took approximately 5 minutes, however the colour of the solution turned dark red almost immediately after the addition began. The formation of the anion can also be followed by infrared spectroscopy. After complete addition of KO^tBu the solution was stirred for an additional few minutes. Completion of the deprotonation was ascertained by IR spectroscopy (anion bands, ν_{CO} 1959(s,br), 1886(s,br) and 1864(sh) cm^{-1}). The extremely air sensitive anion was used immediately for further reactions.

E. Procedures, Chapter 3

Preparation of μ-(η^7-cycloheptatrienyl)tricarbonyl-ruthenium(1,5-cyclooctadiene)rhodium(Ru-Rh), (μ-C_7H_7)Ru(CO)$_3$Rh(COD), 3

A cold (~-78°C) solution of K(η^3-C_7H_7)Ru(CO)$_3$ (2.53 mmol) (obtained from previous preparation) in 100 mL of dry and deoxygenated THF was added dropwise from a jacketed, pressure equalized addition funnel which was cooled with dry ice, over a period of 1.5 h to a magnetically stirred solution of [Rh(COD)Cl]$_2$ (542 mg, 1.23 mmol) in 50 mL THF at room temperature. After the addition was complete, the reaction mixture was allowed to stir at room temperature for an additional 2-3 h. The solvent was removed under vacuum and the residue was extracted with 2 × 30 mL of toluene. The resulting deep red solution was concentrated to 5 mL and placed on a chromatography column packed with silica gel (10 cm × 3 cm). Elution with hexane caused the movement of a deep wine red coloured band which was collected (250 mL) into a one-necked flask under argon. Removal of solvent under vacuum resulted in a deep red crystalline product (350 mg, 28.5%), m.p. 80°C. Elemental analysis: Anal. calcd. for $C_{18}H_{19}O_3RuRh$: C 44.36; H 3.90. Found: C 44.58; H 4.09. Mass spectrum (70 ev, 85°C): 487 (M^+, 53.6%), 459

(M^+-CO, 46.9%), 431 (M^+-2CO, 22.3%), 403 (M^+-3CO, 12.6%). IR (hexane): ν_{CO} 2029(s) and 1965(s) cm^{-1}. ^1H NMR (25°, CD_2Cl_2, 400 MHz): δ 3.75 (s, C_7H_7), 3.6(s br, CH(COD), 4H), 2.7 (m, CH_2(COD) 4H), 2.5(s br, CH_2(COD), 4H). ^{13}C NMR: see Table 6.

Table 6. ^{13}C NMR Data of $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(COD)$, 3.[a]

Temp, °C	δ_{CO}	$\delta_{C_7H_7}$	$\delta_{CH(COD)}$	J_{Rh-C}	$\delta_{CH_2(COD)}$
25	201.6(s)	63.1(s)	80.9(d)	9.2	32.4(s)
-30	201.6(s)	63.1(s)	80.2(d)	9.2	32.8(s)
			79.6(d)	9.1	31.0(s)

[a]Chemical shifts, δ, in ppm from TMS and coupling constants, J, in Hz. Solvent, CD_2Cl_2.

X-ray structure of 3

Dark red crystals of 3, suitable for structural analysis, were obtained by slow crystallization from hexane solution at -20°C. The X-ray structure determination was performed by Dr. R.G. Ball of the Structure Determination Laboratory of this department. Summary of crystallographic data are given in Table 7. Final positional and thermal parameters are listed in Table 8. Additional information can be obtained by

Table 7. Crystallographic Data for $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(COD)$, 3.

Diffractometer	Enraf-Nonius CAD-4F
Temperature, °C	23
Radiation, λ Å	Mo Kα (0.71073)
Monochromator	Incident beam, graphite crystal
Formula	$C_{18}H_{19}O_3RuRh$
Formula weight	487.33
Crystal dimensions, mm	0.17 × 0.10 × 0.27
Crystal system	Orthorhombic
Space group	Pnnm
a, Å	12.277(2)
b, Å	12.658(2)
c, Å	10.868(1)
Volume, $Å^3$	1688.91
Z	4
ρ(calcd), g/cm^3	1.92
Scan type	ω-2θ
Scan rate, deg/min	10.1-1.8
Scan width, deg	0.70 + 0.35 tanθ
2θ limits, deg	54.00
Data collected	1944
Unique data, $I > 3.0\sigma(I)$	1474
Absorption Correction	Yes
Linear abs. coeff. μ, cm^{-1}	18.51
Hydrogens included/refined	Yes/No
No. of parameters refined	119
Agreement factors R, R_w, GOF	0.031/0.043/1.38

Table 8. Table of Positional and Thermal Parameters and Their Estimated Standard Deviations for $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(COD)$, 3.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	2670.9(3)	2053.9(3)	0	37.6(2)	42.5(2)	32.0(2)	-5.4(2)	0	0
Ru	476.7(4)	2875.8(3)	0	41.3(2)	35.3(2)	48.1(2)	-3.7(2)	0	0
O(1)	1097(3)	4408(3)	2032(4)	120(3)	73(2)	88(2)	8(2)	-29(2)	-31(2)
O(2)	-1919(4)	3431(5)	0	55(3)	107(4)	175(6)	20(3)	0	0
C(1)	882(3)	3825(3)	1270(4)	64(3)	45(2)	67(3)	0(2)	-8(2)	-6(2)
C(2)	-1028(5)	3215(5)	0	50(3)	68(4)	86(5)	-2(3)	0	0
C(3)	-1(5)	1234(4)	0	45(3)	30(2)	89(4)	-9(2)	0	0
C(4)	533(3)	1358(3)	1117(4)	54(2)	43(2)	60(2)	-3(2)	13(2)	7(2)
C(5)	1680(3)	1144(3)	1322(4)	57(2)	48(2)	46(2)	-11(2)	2(2)	10(2)
C(6)	2364(3)	453(3)	637(4)	56(2)	41(2)	67(3)	-2(2)	-3(2)	10(2)
C(7)	3664(4)	4195(3)	690(5)	99(3)	74(3)	91(4)	-38(3)	-2(3)	-11(3)
C(8)	3370(3)	3167(3)	1306(4)	55(2)	67(2)	53(2)	-20(2)	-9(2)	-13(2)
C(9)	4004(3)	2260(4)	1295(4)	48(2)	92(3)	48(2)	-5(2)	-14(2)	-7(2)
C(10)	5100(4)	2157(5)	651(5)	48(2)	193(6)	81(4)	4(3)	-9(3)	-9(4)

The atomic positional parameters have been multiplied by 10^4. The anisotropic thermal parameters have been multiplied by 10^3

The form of the anisotropic thermal parameter is:

$$\exp[-2\pi^2(\{h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23}\}]$$

Estimated standard deviations in the least significant digits are shown in parentheses. Those parameters without an error were not refined.

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Preparation of μ-(η^7-cycloheptatrienyl)tricarbonyl-ruthenium(dicarbonyl)rhodium(Ru-Rh), $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2$, **4**

A solution of $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(COD)$ (50 mg, 0.103 mmol) in 30 mL of hexane was cooled to -78°C and degassed. The flask was removed from the cold bath and was put under one atmosphere of carbon monoxide. After warming to room temperature, stirring of the solution was started. The progress of the reaction was followed by infrared spectroscopy in the carbonyl region. After about 0.5 h complete conversion to the pentacarbonyl was seen. The solution was concentrated under vacuum to 5 mL and cooled to -78°C. Removal of the supernatant liquid left behind a red solid which was washed with 10 mL of cold hexane to give analytically pure **4** as a red solid (40 mg, 90%). Anal. calcd. for $C_{12}H_7O_5RuRh$: C 33.12; H 1.61. Found: C 33.27; H 1.72. Mass spectrum (70 ev, 80°C): M^+, M^+-nCO (n = 1 to 5). IR (hexane): ν_{CO} 2064(s), 2023(s), 2004(s), 1979(s), and 1965(s) cm^{-1}. ^1H NMR (25°, CD_2Cl_2, 400 MHz): δ 4.10 (s, C_7H_7). ^{13}C NMR (25°, d_8-toluene, 100.6 MHz): δ 61.3 (s, C_7H_7), 194.5 (d, CO_{Rh}, J_{Rh-C} = 72 Hz), 200.6 (s, CO_{Ru}).

Preparation of ^{13}CO-enriched sample of 4

50 mg of $(\mu\text{-}C_7H_7)Rh(CO)_2Ru(CO)_3$, 4, was dissolved in 20 mL of hexane in a 100 mL one-necked flask (the neck consisted of a straight Teflon Rotaflow tap). The flask was cooled to -78°C and degassed. The flask was removed from the cold bath and was put under one atmosphere of ^{13}CO, and the solution was stirred well for 0.5 h while the flask warmed up to room temperature. The enrichment was followed by IR spectroscopy. After 0.5 h approximately 90% enrichment was observed, as judged by mass spectrometric analysis.

F. Procedures, Chapter 4

Synthesis of μ-(η^7-cycloheptatrienyl)tricarbonylruthenium carbonyl(triphenylphosphine)rhodium(Ru-Rh), $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)PPh_3$, 5

Triphenylphosphine (30.0 mg, 0.114 mmol) was added directly as a solid to a stirred solution of $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)$ (50.0 mg, 0.115 mmol) in 30 mL of hexane at room temperature. Stirring was continued for 0.5 h which caused the solution to become a deeper red. Upon concentration under vacuum a red solid precipitated. Inverse filtration, followed by washing

with cold hexane and drying in vacuum gave 62 mg (92%) of **5** as a red solid. Anal. calcd. for $C_{29}H_{22}O_4PRuRh$: C 52.02; H 3.29. Found: C 52.34; H 3.44. Mass spectrum (70 ev, 165°C): M^+, M^+-nCO (n = 1-4). ^1H NMR (25°C, CD_2Cl_2, 400 MHz): δ 3.9 (s, C_7H_7), 7.3-7.4 (m, C_6H_5). ^{13}C NMR (CD_2Cl_2, 100.6 MHz) (25°C): δ65.1 (s, C_7H_7), 137-135 (C_6H_5), 216.6 (br, CO). (-30°C): δ217.0 (s, CO_{Ru}), 202.5 (d,d, CO_{Rh}, J_{Rh-C} = 87.8 Hz, J_{P-C} = 15.8 Hz). ^{31}P NMR (25°C, CD_2Cl_2. 161 MHz): δ 40.88 (d, P_{Rh}, J_{Rh-P} = 183.3 Hz).

Preparation of ^{13}CO-enriched sample of **5**

Triphenylphosphine (17.8 mg, 0.068 mmol) was added directly as a solid to a stirred solution of ^{13}CO enriched pentacarbonyl **4** (30 mg, 0.068 mmol) in 20 mL hexane. Stirring was continued for 0.5 h and the IR of the solution showed complete conversion to compound **5**. The material was isolated as described earlier for the unenriched compound **5**.

Preparation of μ-(η^7-cycloheptatrienyl)(μ-bis-diphenylphosphinomethane)dicarbonylruthenium(carbonyl)-rhodium(Ru-Rh), (μ-C_7H_7)(μ-DPPM)$Ru(CO)_2Rh(CO)$, **6**

Bisdiphenylphosphinomethane (44.0 mg, 0.115 mmol) was

added directly as a solid to a stirred solution of $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2$ (50.0 mg, 0.115 mmol) in 20 mL of hexane at room temperature. After a few minutes a deep red solid precipitated. The solid was isolated by inverse filtration. Washing with cold pentane and drying in vacuum gave 65 mg (85%) of **6** as a red solid. Anal. calcd. for $C_{35}H_{29}RuO_3P_2Rh$: C 55.04; H 3.80. Found: 55.10; H 4.03. Mass spectrum (70 ev, 125°C): M^+-CO, M^+-2CO, M^+-3CO. IR (CD_2Cl_2): ν_{CO} 1975(s), 1940(s), and 1904(br) cm^{-1}. ^1H NMR (-80°C, CD_2Cl_2, 400 MHz): δ 3.9(s, C_7H_7); 4.05 (q, CH_2, 1H, J_{H-H} = 10 Hz), 1.95 (q, CH_2, 1H, J_{H-H} = 10 Hz); 7.2-7.4 (m, C_6H_5). ^{13}C NMR (25°C, CD_2Cl_2, 100.6 MHz): δ 61.0(s, C_7H_7), 125-128 (C_6H_5), 204.9 (br s, CO_{Ru}), 201.7 (d,d, CO_{Rh}, J_{Rh-C} = 77.7 Hz, J_{P-C} = 12.4 Hz). At -75°C CO_{Ru} appear at 209.6(s), 199.7 (d, J_{P-C} = 7.0 Hz). ^{31}P NMR (25, CD_2Cl_2, 161 MHz): ABX pattern, P_{Ru}: δ70.58 (J_{P-P} = 139.4 Hz, J_{Rh-P} = 2.3 Hz), P_{Rh}: δ 68.41 (J_{P-P} = 139.4 Hz, J_{Rh-P} = 154.5 Hz).

Preparation of ^{13}CO-enriched sample of **6**

Compound **6** (30 mg) was dissolved in 20 mL of methylene chloride in a 100 mL one-necked flask. (The neck consisted of a straight Teflon rotaflow tap.) The flask was cooled and degassed. The flask was removed from the cold bath and was put under one atmosphere of ^{13}CO and

the solution was stirred for 0.5 h, while the flask warmed up to room temperature. The enrichment was followed by IR spectroscopy until all the starting material disappeared. Solid **6** precipitated as the solution was concentrated. The solid was isolated by inverse filtration and dried under vacuum.

^{31}P NMR studies of the reaction of $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2$ with DPPM

$(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2$ **4** (20 mg, 0.046 mmol) was dissolved in 0.25 mL of CD_2Cl_2 in a NMR tube under a nitrogen atmosphere. The solution was cooled to -50°C by placing the tube in an acetone-dry ice bath. DPPM (17 mg, 0.046 mmol) was dissolved separately in 0.25 mL of CD_2Cl_2. The DPPM solution was added to **4** at -50°C. The combined solution was mixed well and immediately placed in the NMR probe maintained at -50°C. Spectra were recorded as the temperature was raised from -50°C to room temperature over a period of 3 hours.

Several experiments were carried out in a similar fashion. It was found that to obtain reproducible results and spectra as shown in Figure 10 of Chapter 4, it was imperative that all free DPPM was consumed during the mixing period. Otherwise more complicated NMR spectra

were obtained which showed some of the features seen in the spectra which were obtained when the reagents were mixed at -80°C.

Experiments were also conducted by keeping and mixing the individual solutions at -80°C. In these runs the initial ^{31}P NMR spectrum was recorded at -80°C as well.

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